



US009428690B2

(12) **United States Patent**
Gu et al.

(10) **Patent No.:** **US 9,428,690 B2**

(45) **Date of Patent:** ***Aug. 30, 2016**

(54) **YELLOW-GREEN TO YELLOW-EMITTING
PHOSPHORS BASED ON
TERBIUM-CONTAINING ALUMINATES**

(71) Applicant: **Intematix Corporation**, Fremont, CA
(US)

(72) Inventors: **Jingtao Gu**, Shanghai (CN); **Chengjun
Duan**, Changshu (CN); **Yi-Qun Li**,
Danville, CA (US)

(73) Assignee: **Intematix Corporation**, Fremont, CA
(US)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-
claimer.

(21) Appl. No.: **14/837,459**

(22) Filed: **Aug. 27, 2015**

(65) **Prior Publication Data**

US 2016/0115385 A1 Apr. 28, 2016

Related U.S. Application Data

(63) Continuation of application No. 14/513,133, filed on
Oct. 13, 2014, now Pat. No. 9,120,975, which is a
continuation of application No.
PCT/CN2012/087751, filed on Dec. 28, 2012, and a

(Continued)

(51) **Int. Cl.**
C09K 11/77 (2006.01)
F21K 99/00 (2016.01)
F21V 9/16 (2006.01)

(52) **U.S. Cl.**
CPC **C09K 11/7774** (2013.01); **C09K 11/777**
(2013.01); **F21K 9/56** (2013.01); **F21V 9/16**
(2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,037,577 A 8/1991 Yamanoi et al.
5,600,202 A 2/1997 Yamada et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN 1254747 5/2000
CN 1318271 A 10/2001

(Continued)

OTHER PUBLICATIONS

International Search Report and Written Opinion Issued Oct. 3,
2013 for PCT/CN2012/08775.

(Continued)

Primary Examiner — Melvin C Mayes

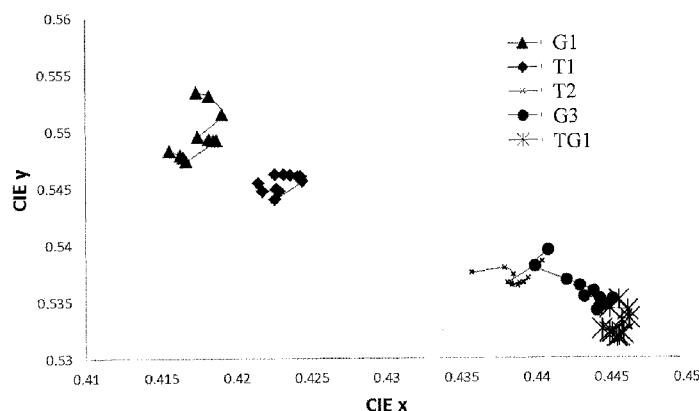
Assistant Examiner — Stefanie Cohen

(74) *Attorney, Agent, or Firm* — David H. Jaffer; Pillsbury
Winthrop Shaw Pittman LLP

(57) **ABSTRACT**

Yellow-green to yellow-emitting, lutetium aluminate-based
terbium (Tb) containing phosphors for use in white LEDs,
general lighting, and LED and backlighting displays are
disclosed herein. The phosphor may further contain gad-
olinium (Gd). In one embodiment of the present invention,
the phosphor comprises a cerium-activated, yellow-green to
yellow-emitting lutetium aluminate-based phosphor having
the formula $(\text{Lu}_{1-x}\text{A}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$ wherein A is at least one
of Gd and Tb and $0.1 \leq x \leq 1.0$, wherein the phosphor is
configured to emit light having a peak emission wavelength
ranging from about 550 nm to about 565 nm, and wherein
the phosphor contains at least some Tb.

19 Claims, 15 Drawing Sheets



Related U.S. Application Data

continuation-in-part of application No. 13/931,214, filed on Jun. 28, 2013, now Pat. No. 8,877,094, which is a continuation of application No. 13/415,623, filed on Mar. 8, 2012, now Pat. No. 8,475,683.

- (60) Provisional application No. 61/450,310, filed on Mar. 8, 2011.

- (56) **References Cited**

U.S. PATENT DOCUMENTS

5,998,925	A	12/1999	Shimizu et al.	
6,013,199	A	1/2000	McFarland et al.	
6,069,440	A	5/2000	Shimizu et al.	
6,245,259	B1	6/2001	Hohn et al.	
6,409,938	B1	6/2002	Comanzo	
6,577,073	B2	6/2003	Shimizu et al.	
6,669,866	B1	12/2003	Kummer et al.	
6,869,544	B2	3/2005	Chen et al.	
7,029,602	B2	4/2006	Oshio	
7,267,786	B2	9/2007	Fiedler et al.	
7,311,858	B2	12/2007	Wang	
7,521,862	B2	4/2009	Mueller et al.	
7,573,072	B2	8/2009	Setlur et al.	
7,575,697	B2	8/2009	Li et al.	
7,753,553	B2	7/2010	Justel et al.	
8,274,215	B2	9/2012	Liu et al.	
8,475,683	B2 *	7/2013	Li	C09K 11/7774 252/301.4 H
8,529,791	B2	9/2013	Wu et al.	
8,877,094	B2 *	11/2014	Li	C09K 11/7774 252/301.4 H
9,120,975	B2 *	9/2015	Gu	C09K 11/0883
2003/0001495	A1	1/2003	Liu et al.	
2003/0203205	A1	10/2003	Bi et al.	
2004/0000862	A1	1/2004	Setlur et al.	
2004/0084655	A1	5/2004	Vartuli et al.	
2004/0173807	A1	9/2004	Tian et al.	
2004/0256974	A1	12/2004	Mueller-Mach et al.	
2005/0092408	A1	5/2005	Lauf et al.	
2005/0093442	A1	5/2005	Setlur et al.	
2005/0141240	A1	6/2005	Hata et al.	
2005/0142240	A1	6/2005	Chiu et al.	
2005/0145868	A1	7/2005	Kummer et al.	
2005/0199897	A1	9/2005	Setlur et al.	
2005/0242329	A1	11/2005	Fiedler et al.	
2006/0028122	A1	2/2006	Wang et al.	
2006/0083694	A1	4/2006	Kodas et al.	
2006/0158097	A1	7/2006	Juestel et al.	
2006/0164005	A1	7/2006	Sun	
2008/0018235	A1	1/2008	Wang et al.	
2008/0064586	A1	3/2008	Mitomo et al.	
2008/0116788	A1	5/2008	Yamazaki et al.	
2008/0138268	A1	6/2008	Tao et al.	
2008/0203892	A1	8/2008	Schmidt et al.	
2008/0231171	A1	9/2008	Schmidt et al.	
2008/0296596	A1	12/2008	Setlur et al.	
2009/0008663	A1	1/2009	Shimizu et al.	
2009/0066221	A1	3/2009	Schmidt et al.	
2009/0072255	A1	3/2009	Takahashi et al.	
2009/0072710	A1	3/2009	Schmidt et al.	
2009/0174310	A1	7/2009	Vogt et al.	
2009/0212314	A1	8/2009	Im et al.	
2009/0218585	A1	9/2009	Zhuang et al.	
2009/0243467	A1	10/2009	Shimizu et al.	
2010/0059681	A1	3/2010	Nakamura et al.	
2010/0085728	A1	4/2010	Seto et al.	
2010/0225226	A1	9/2010	Murazaki et al.	
2010/0308712	A1	12/2010	Liu et al.	
2011/0050086	A1	3/2011	Liu et al.	
2011/0175028	A1	7/2011	Shimamura et al.	
2011/0279022	A1	11/2011	Winkler et al.	

2011/0305005	A1	12/2011	Tsukatani et al.
2012/0112130	A1	5/2012	Wu et al.
2013/0001444	A1	1/2013	Zhou et al.

FOREIGN PATENT DOCUMENTS

CN	1478855	A	3/2004
CN	1629251		6/2005
CN	1995274	A	7/2007
CN	100999662		7/2007
CN	10137738	A	3/2008
CN	10182416	A	5/2008
CN	10136522		3/2009
CN	101638578		2/2010
CN	101760196	A	6/2010
CN	102687266		9/2012
CN	102723422		10/2012
DE	19934126		1/2001
DE	10 2008 051029	A1	4/2010
EP	1378556		1/2004
EP	1589090		10/2005
JP	H0673376	A	3/1994
JP	H10-247750		9/1998
JP	H10242513	A	9/1998
JP	2004115633	A	4/2004
JP	2004-168996		10/2004
JP	2005008844	A	1/2005
JP	2005-120251	A	5/2005
JP	2006-041096	A	2/2006
JP	2006265542	A	10/2006
JP	2006-299168	A	11/2006
JP	2008189811	A	8/2008
JP	2008291203	A	12/2008
JP	2010-121068	A	6/2010
JP	2011249829	A	12/2011
KR	1002007-0106536	A	11/2007
TW	2006193586	A	6/2006
WO	WO2004/084261		9/2004
WO	WO 2005/061659	A1	7/2005
WO	WO2005123876	A	12/2005
WO	WO2006/129559		12/2006
WO	WO2008056292	A1	5/2008
WO	WO2010053197	A1	5/2010
WO	WO2010/074963	A1	7/2010
WO	WO2012/122401	A2	9/2012

OTHER PUBLICATIONS

Kuru, et al., "Yttrium Aluminum Garnet as a Scavenger for Ca and Si", J. of the American Ceramic Soc., 2008, vol. 91, No. 11, pp. 3663-3667.

Kim, et al., "Synthesis and Luminescent Characterization of Zinc Thiogallant", J. of Europ. Ceramic Soc., Mar. 26, 2007, Vo. 27, pp. 3667-3670.

Li, K., et al., "Relationship between Crystal Structure and Luminescence Properties of $(Y_{0.96-x}Ln_{x}Ce_{0.04})_3Al_5O_{12}$ ($Ln = Gd, La, Lu$) Phosphors," *Journal of Rare Earths* vol. 25, 2007, pp. 692-696.

Li, et al., "Fabrication of Transparent Cerium-doped Lutetium Aluminum Garnet Ceramics by co-Precipitation Routes", J. of the American Ceramic Soc., 2006, vol. 89, No. 7, pp. 2356-2358.

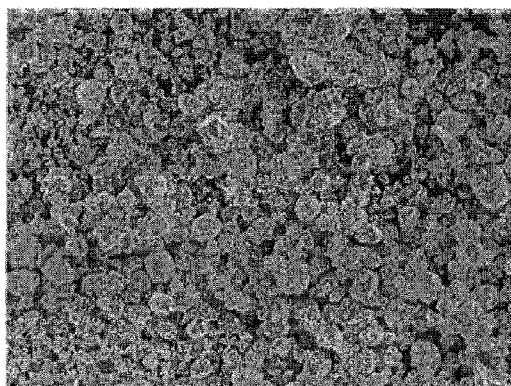
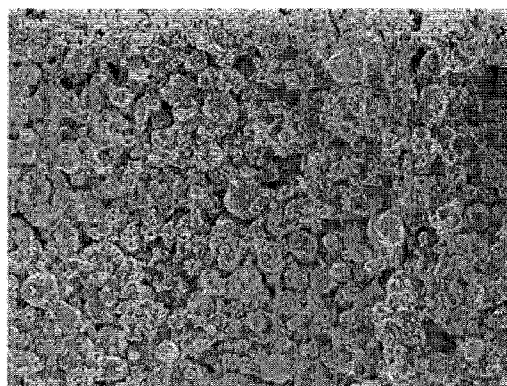
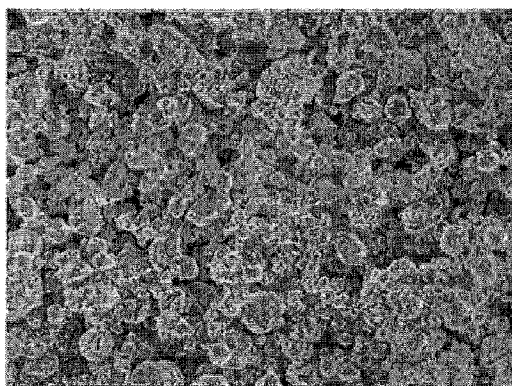
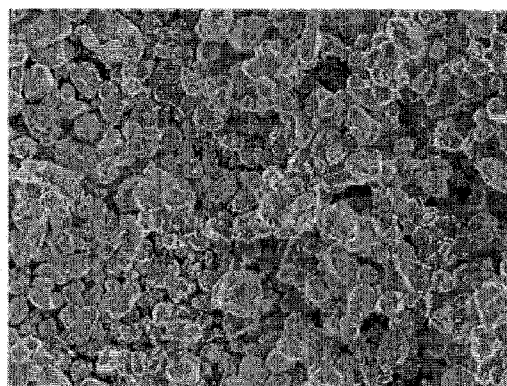
Baccaro, et al., "Influence of Si-codoping on YAG:Ce Scintillation Characteristics", IEEE Trans. On Nuclear Science, Aug. 2005, pp. 1105-1108, vol. 52, No. 4.

Fernandez, et al., "Highly Porous Yttrium Aluminum Garnet (YAG) Particles Synthesized by a Gel Supported Precipitation (GSP) Process," J. of Mat. Sci., Jan. 2003, pp. 2331-2335, vol. 38.

Phosphors for Application in White GaN-based LEDs, Mats, Research Soc. Symp. Proc., Jan. 1, 2001, vol. 658, pp. GG11.8.1-GG.11.8.6.

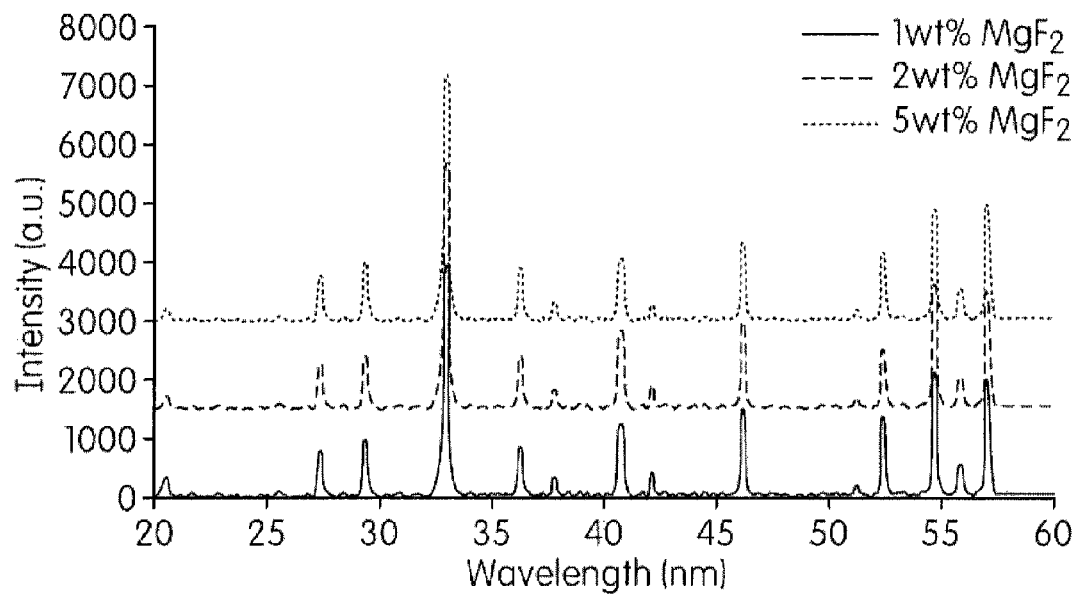
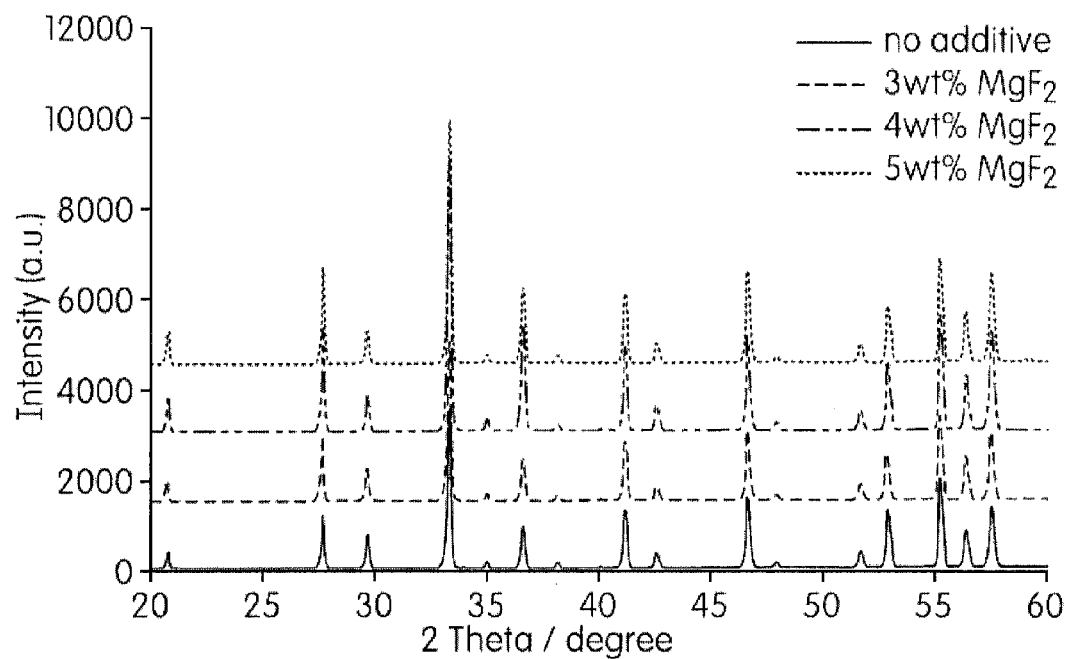
Kang, et al., "YAG:Ce Phosphor Particles prepared by Ultrasonic Spray Pyrolysis", Mats. Research bull., 2000, pp. 789-798.

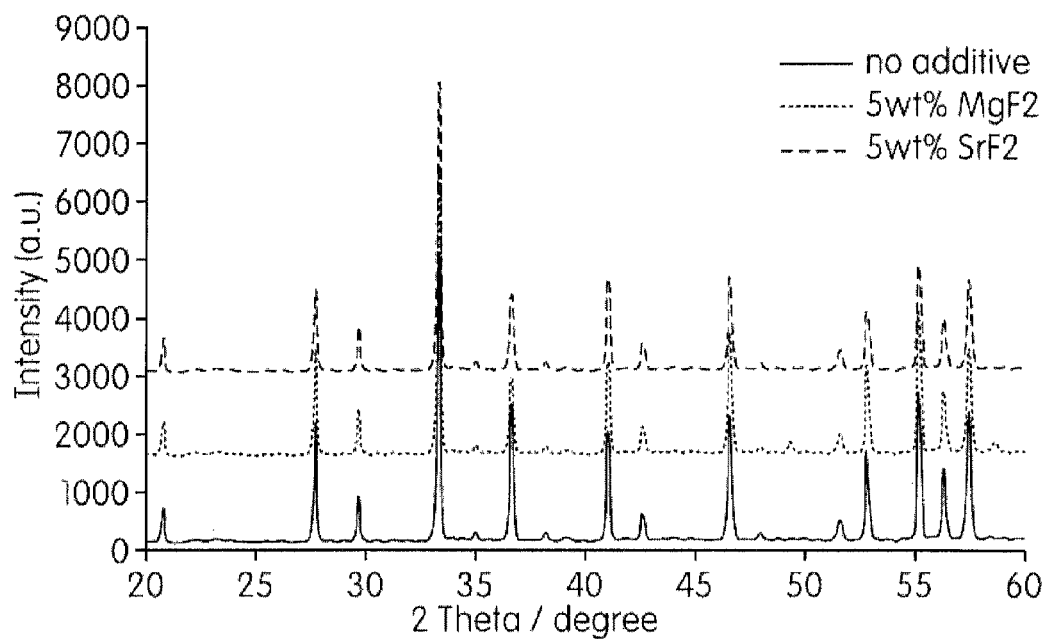
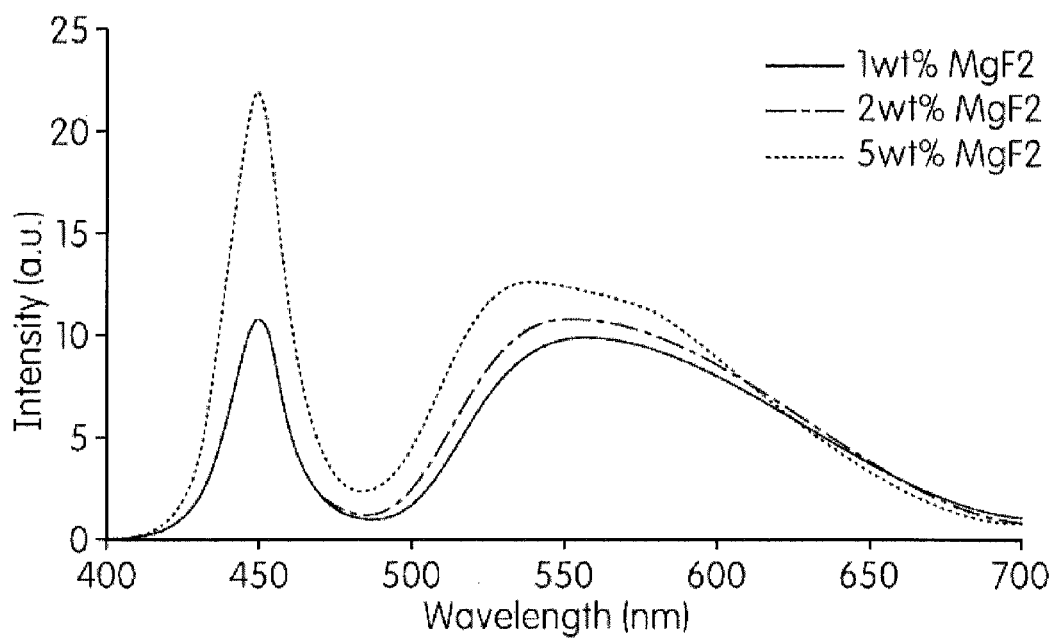
* cited by examiner

2 wt% MgF₂3 wt% MgF₂4 wt% MgF₂5 wt% MgF₂

SEM Morphology of Lu_{2.91}Ce_{0.09}Al₅O₁₂ with
different MgF₂ additive concentrations

FIG. 1

**FIG. 2****FIG. 3**

**FIG. 4****FIG. 5**

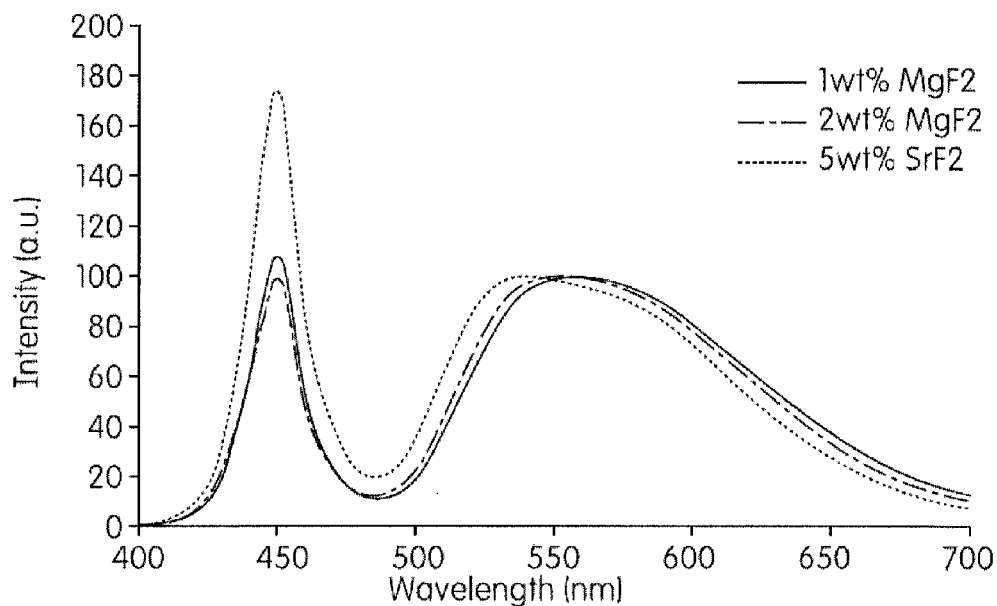


FIG. 6

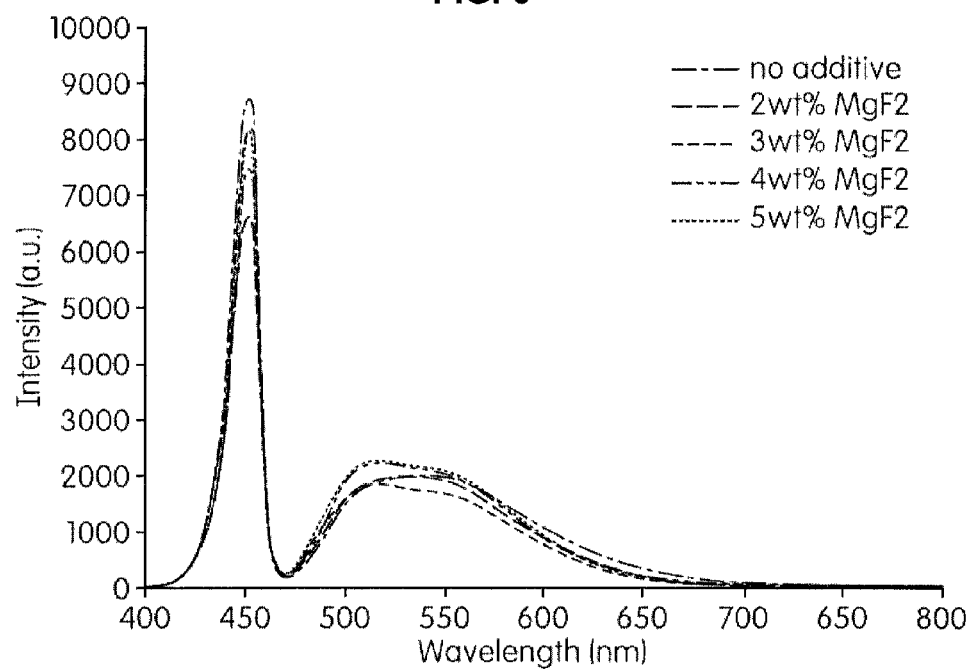
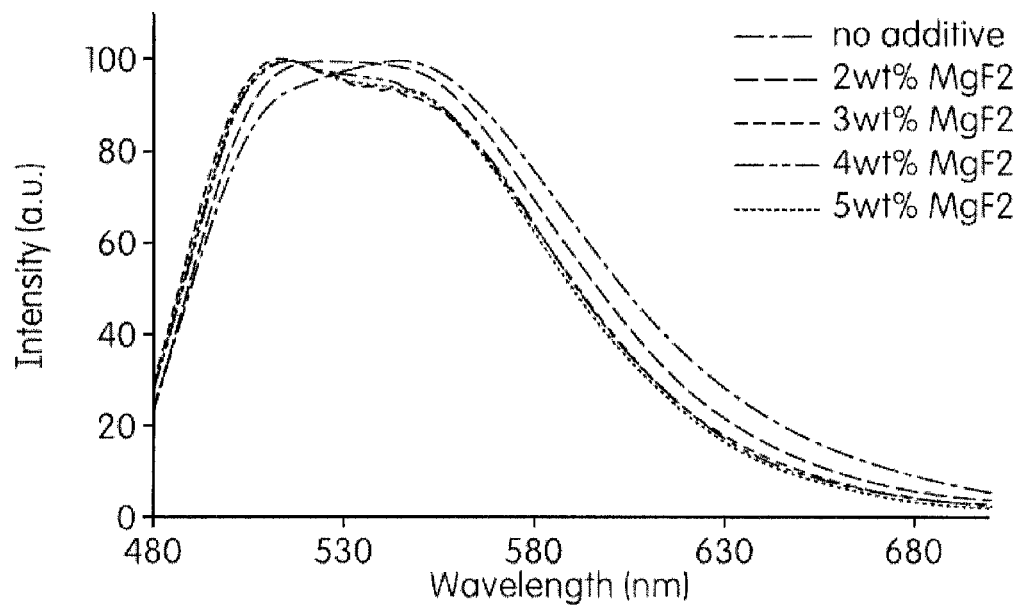
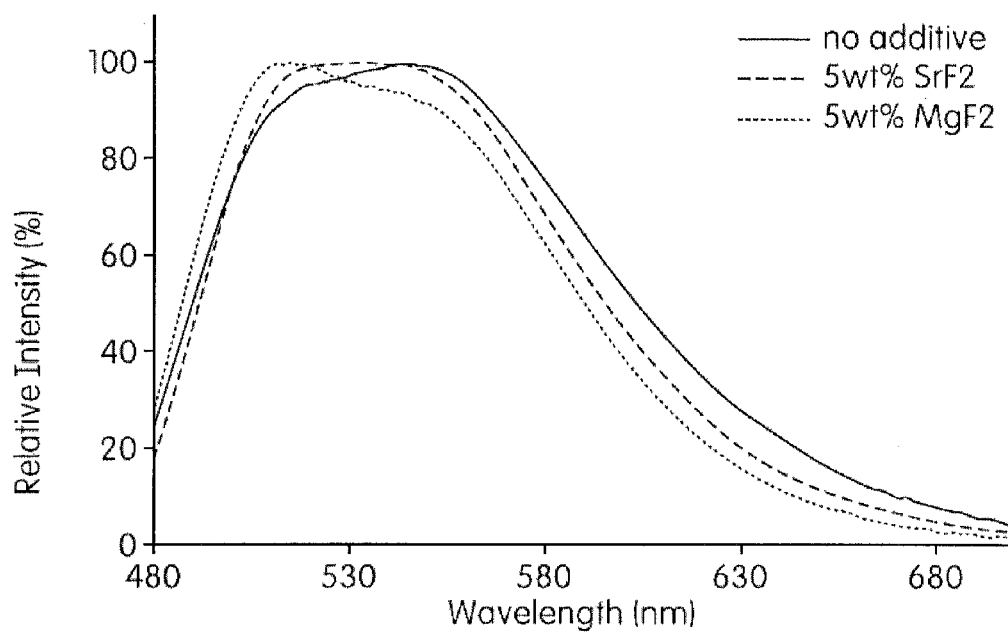
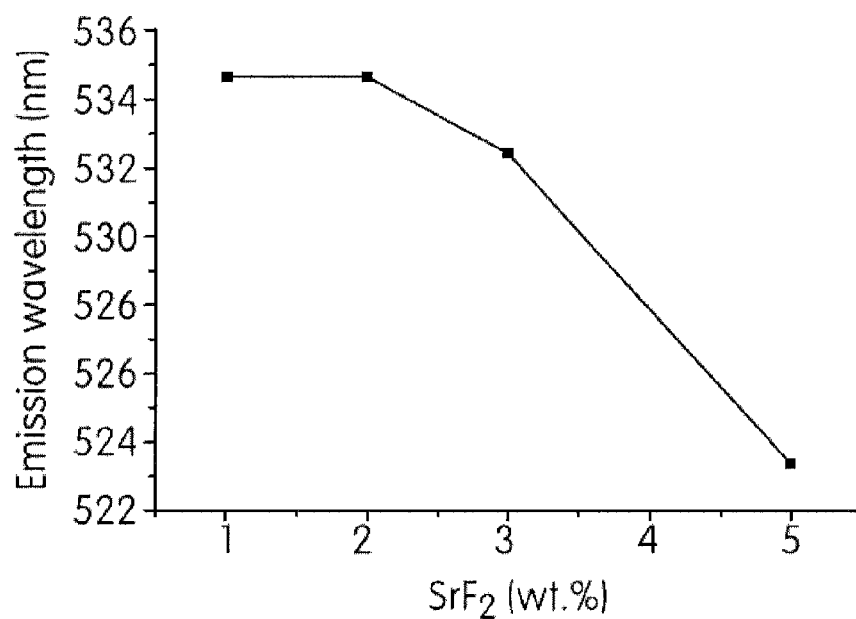
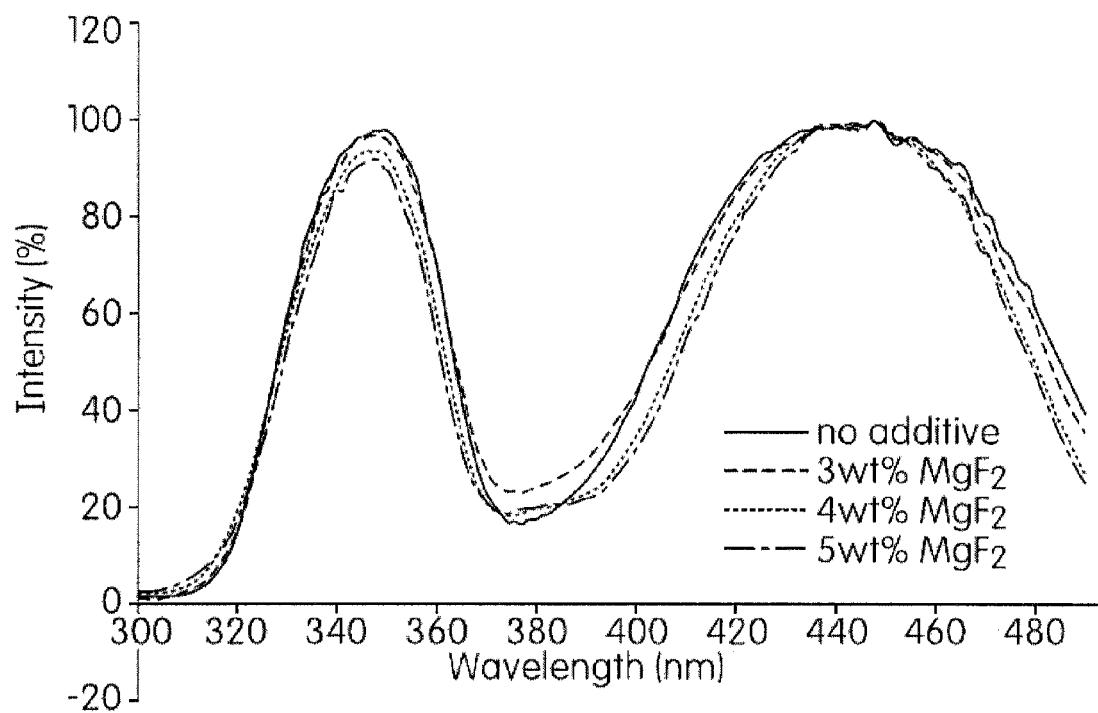


FIG. 7

**FIG. 8****FIG. 9**

**FIG. 10****FIG. 11**

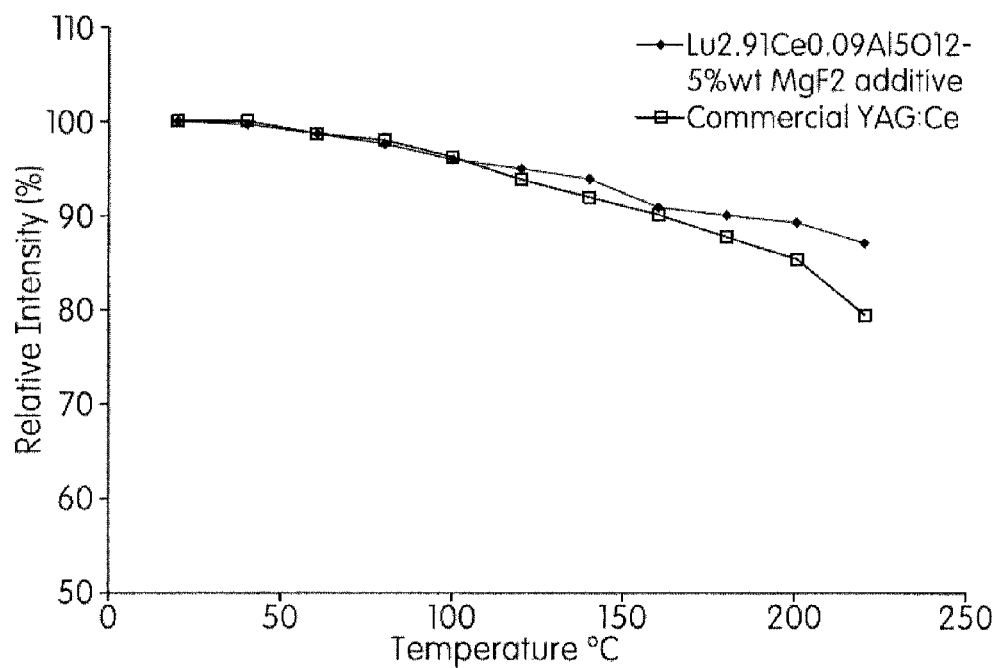


FIG. 12

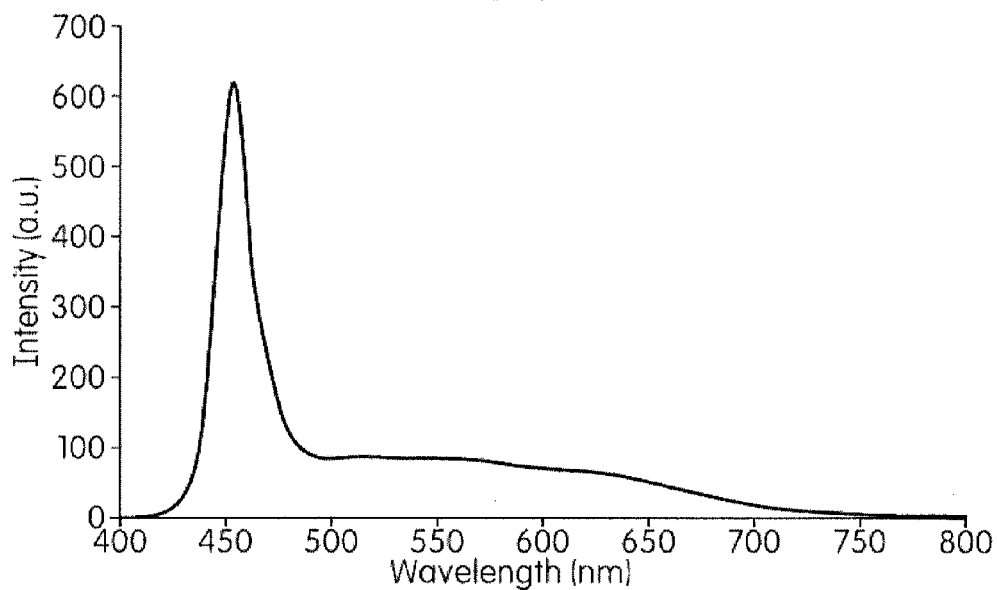


FIG. 13

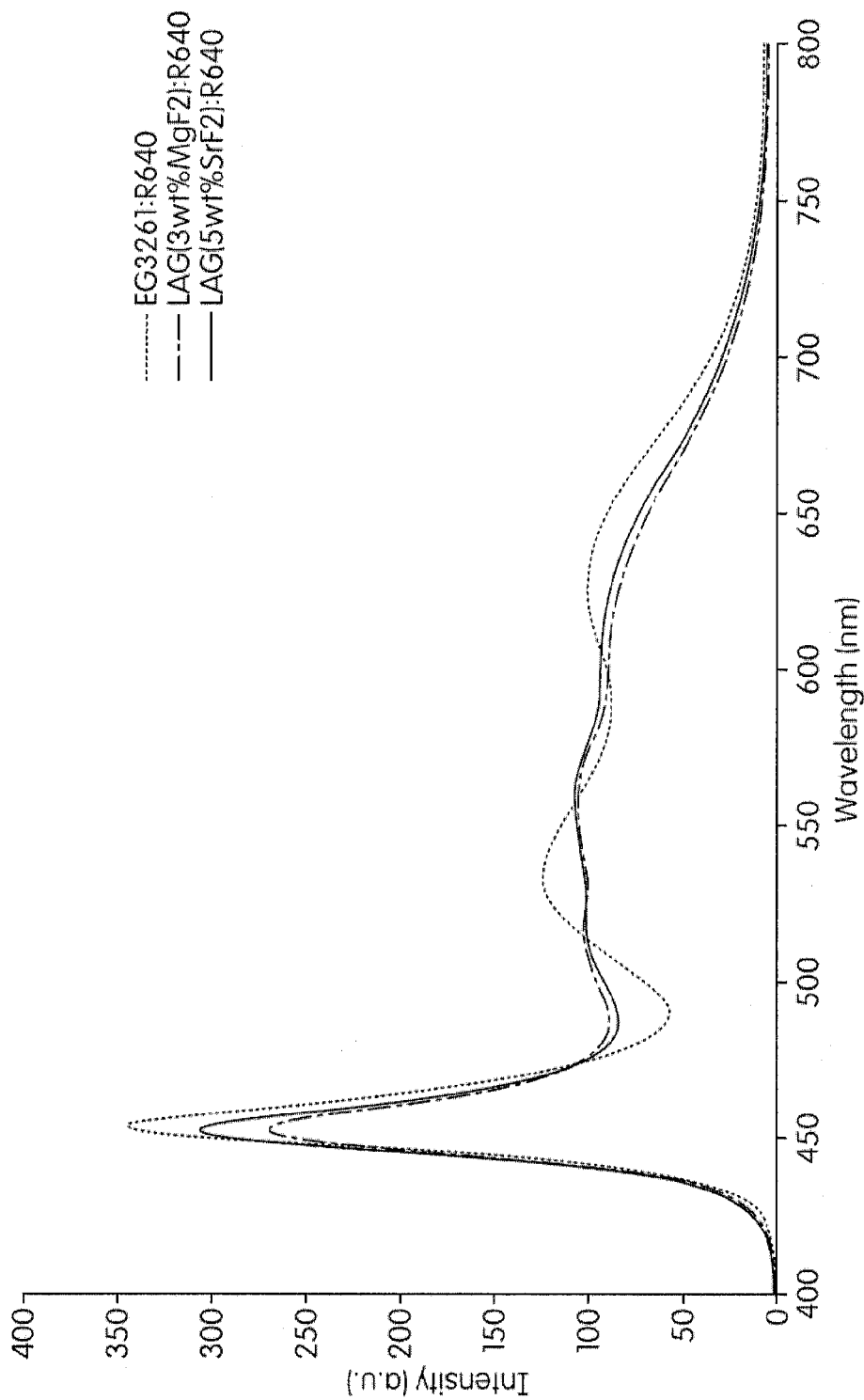


FIG. 14

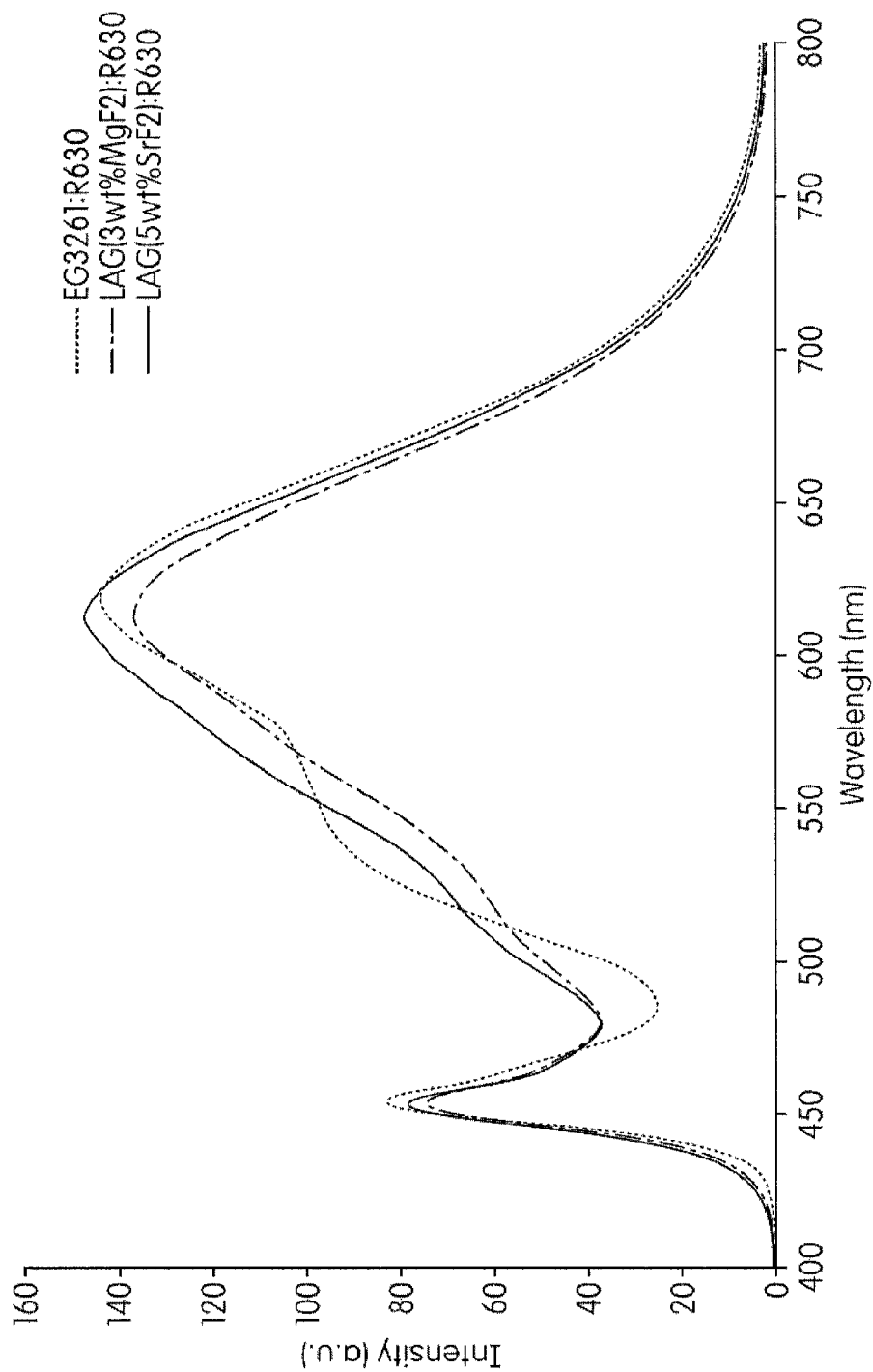


FIG. 15

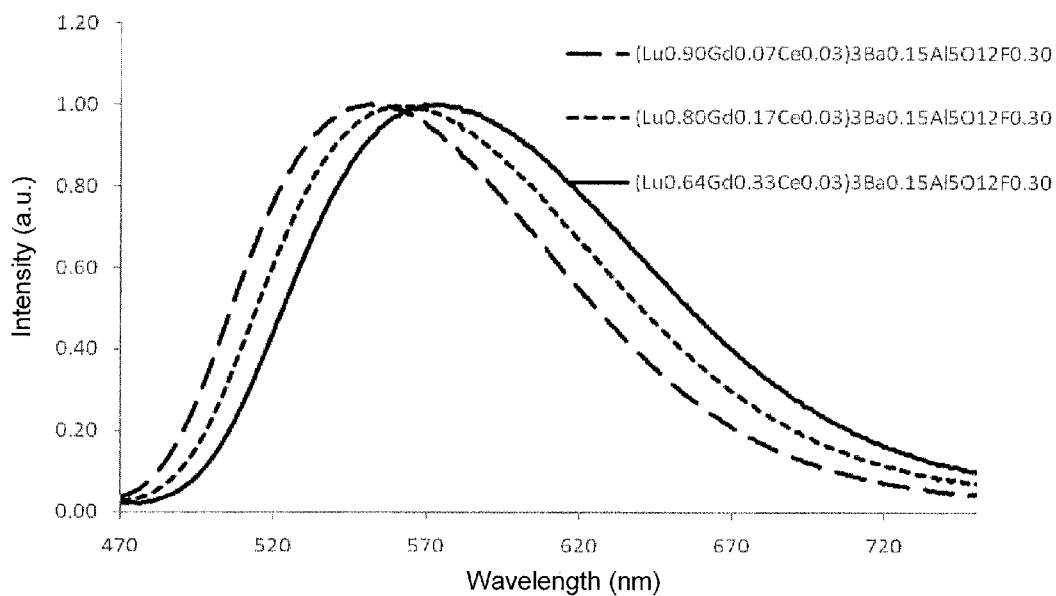


FIG. 16A

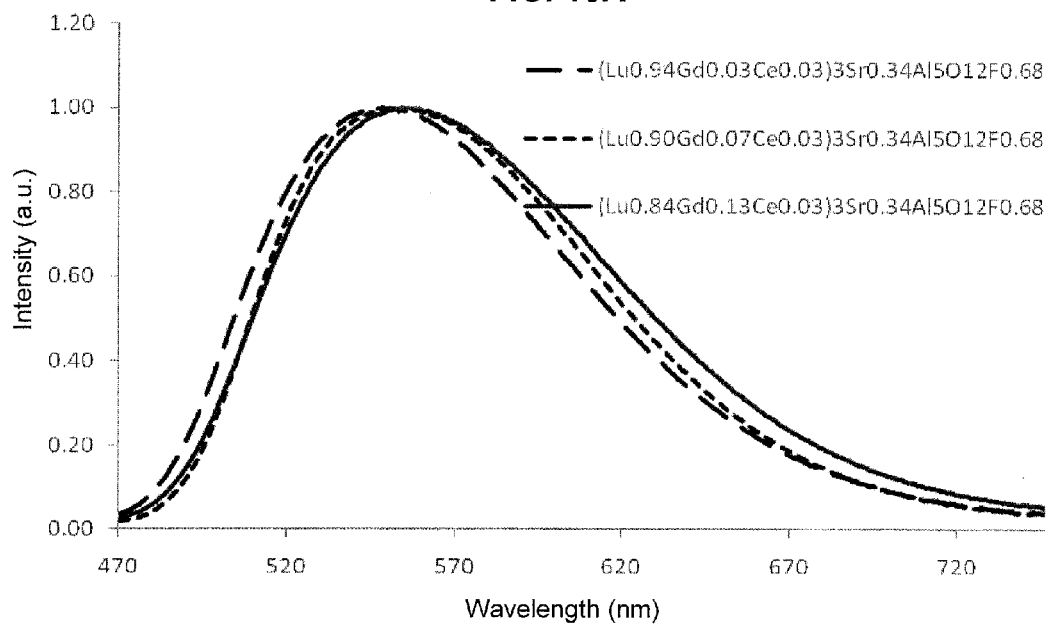
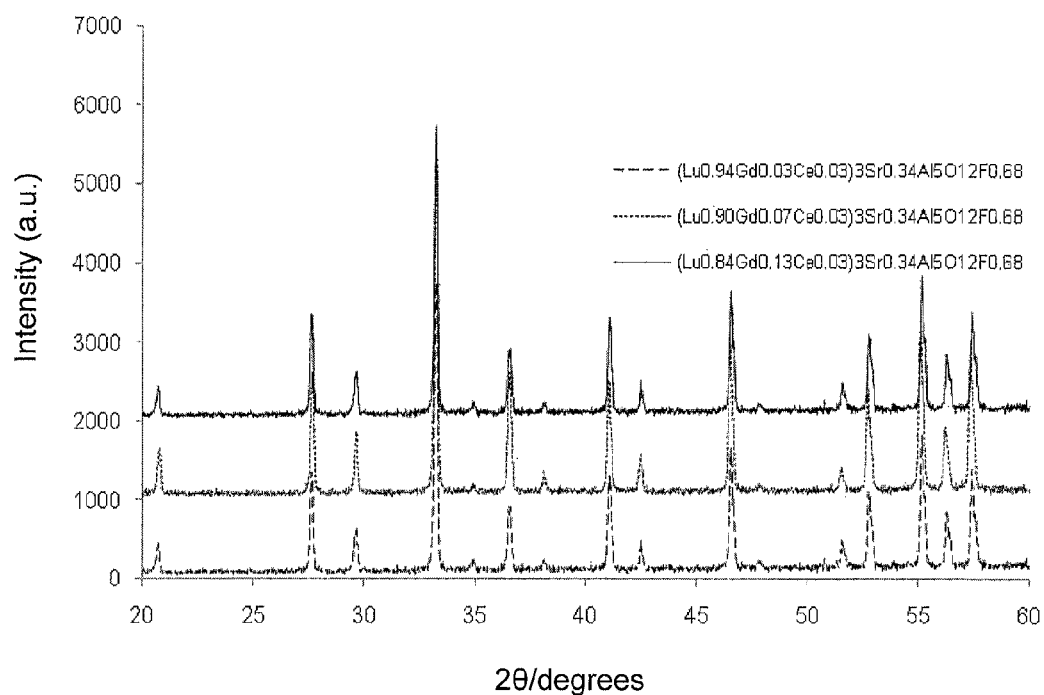
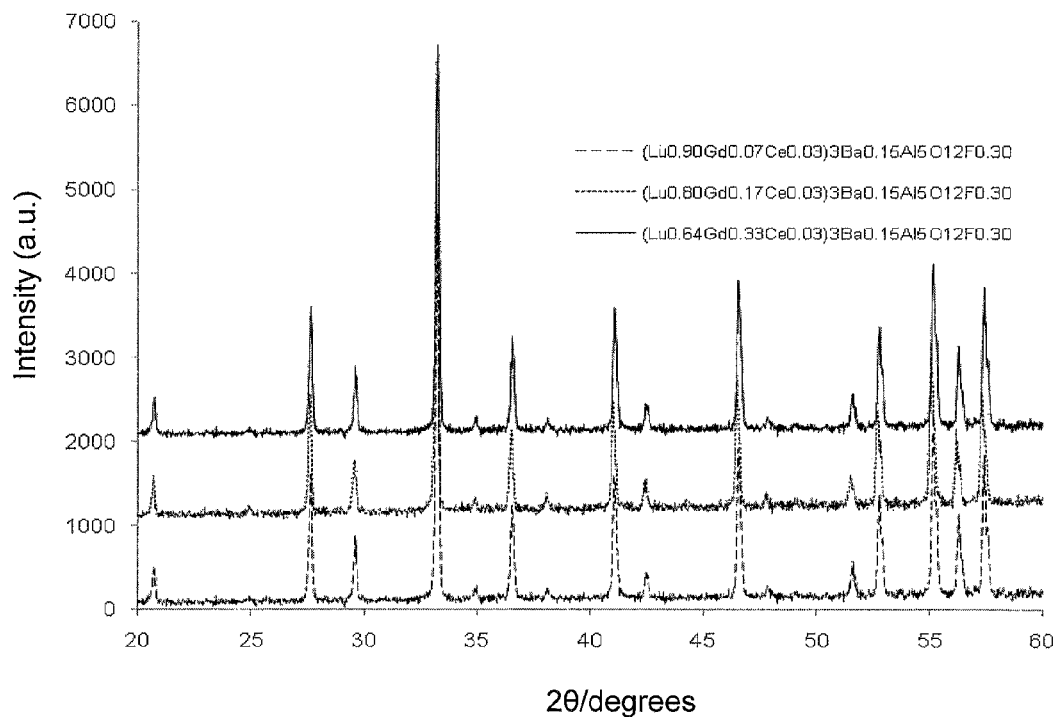
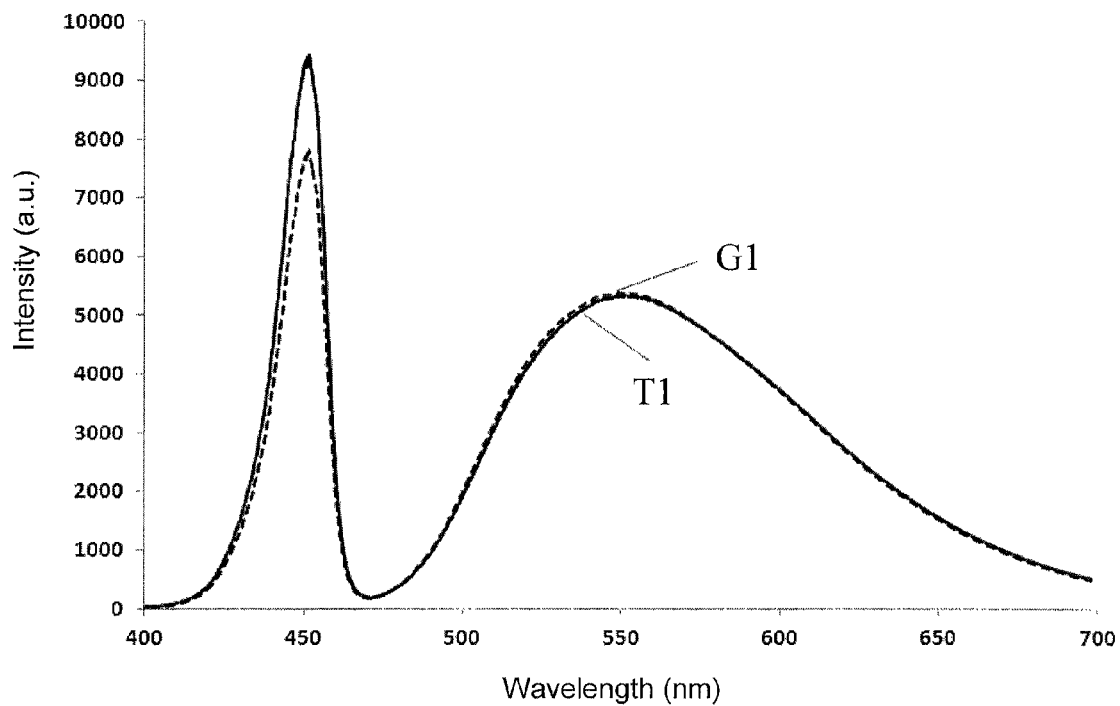
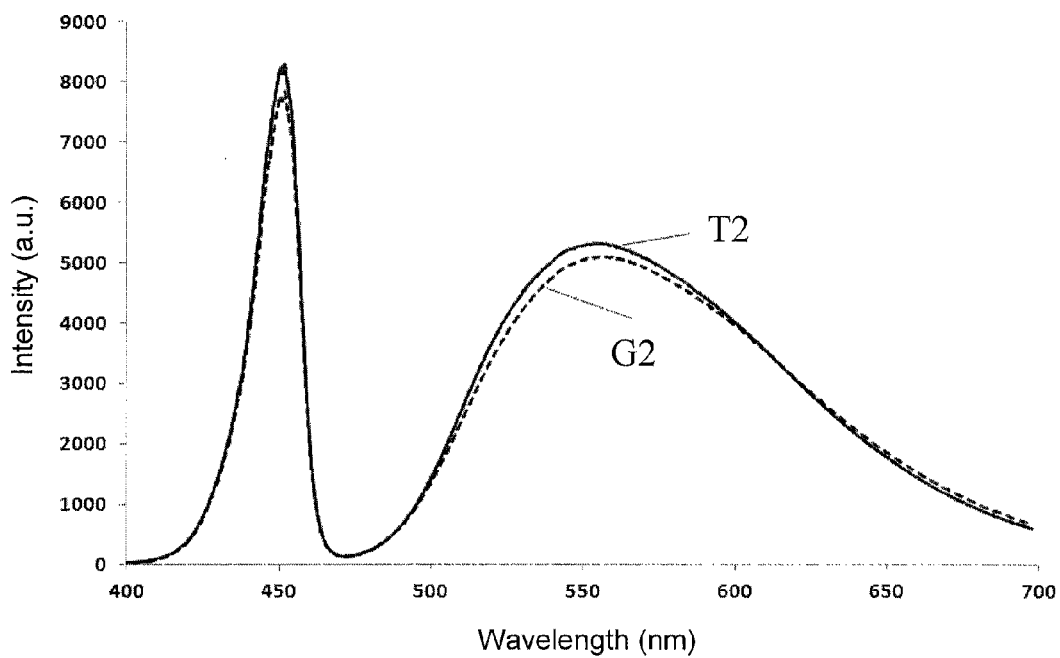
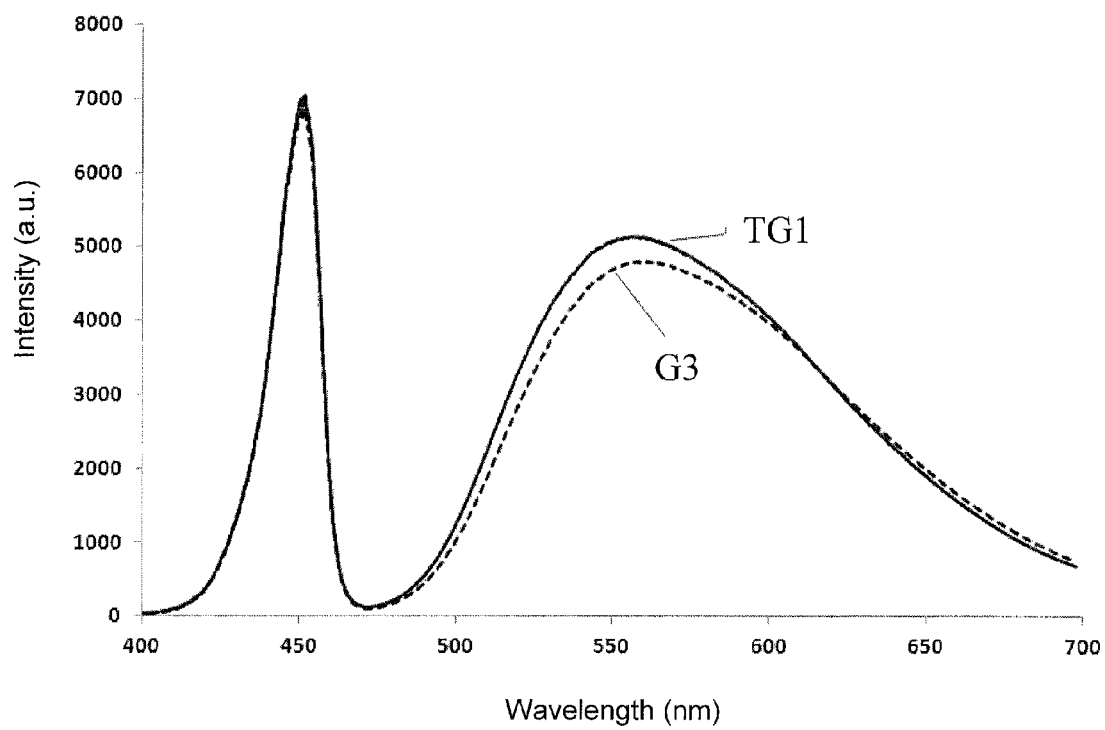


FIG. 16B

**FIG. 17A****FIG. 17B**

**FIG. 18****FIG. 19**

**FIG. 20**

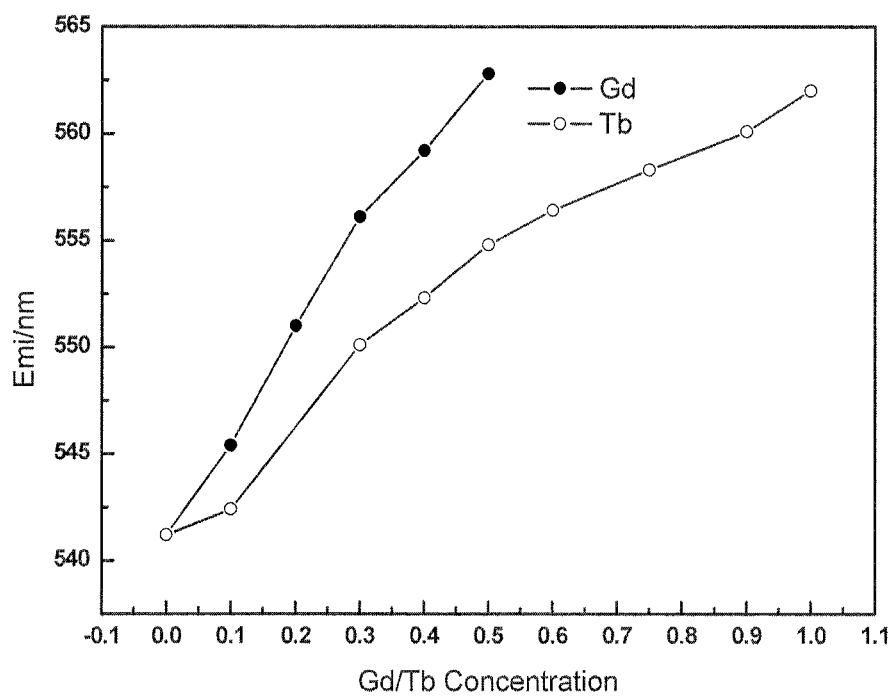


FIG. 21

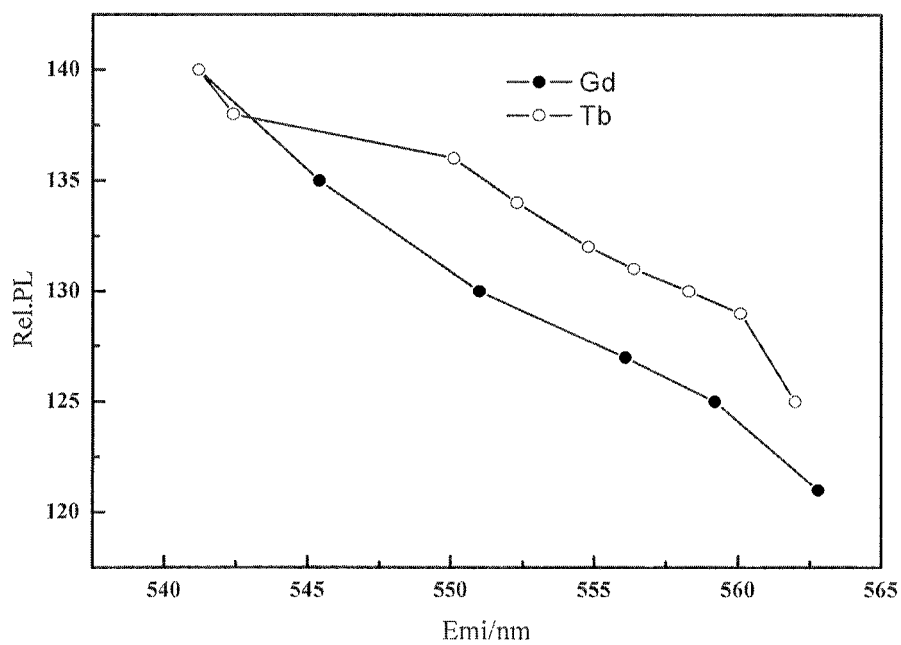


FIG. 22

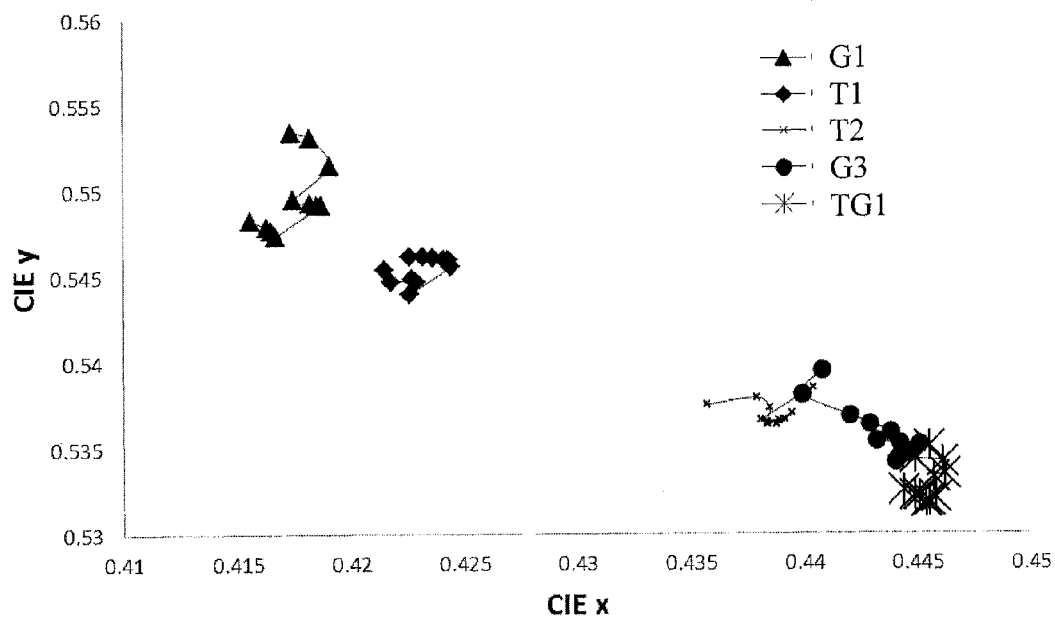


FIG. 23

YELLOW-GREEN TO YELLOW-EMITTING PHOSPHORS BASED ON TERBIUM-CONTAINING ALUMINATES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 14/513,133 filed Oct. 13, 2014 entitled YELLOW-GREEN TO YELLOW-EMITTING PHOSPHORS BASED ON TERBIUM-CONTAINING ALUMINATES by Jingtao Gu et al., (now U.S. Pat. No. 9,120,975) which is a continuation of PCT Application No. PCT/CN2012/087751 with an international filing date of Dec. 28, 2012 entitled YELLOW-GREEN TO YELLOW-EMITTING PHOSPHORS BASED ON TERBIUM-CONTAINING ALUMINATES by Jingtao Gu et al., now published as WO 2014/101073 A1, and is also a continuation-in-part of U.S. patent application Ser. No. 13/931,214 filed June 28, 2013, entitled YELLOW-GREEN TO YELLOW-EMITTING PHOSPHORS BASED ON HALOGENATED-ALUMINATES, by Yi-Qun Li et al., now U.S. Pat. No. 8,877,094, which is a continuation of U.S. patent application Ser. No. 13/415,623 filed Mar. 8, 2012, now U.S. Pat. No. 8,475,683, entitled YELLOW-GREEN TO YELLOW-EMITTING PHOSPHORS BASED ON HALOGENATED-ALUMINATES, by Yi-Qun Li et al., which claims the benefit of U.S. Provisional Application No. 61/450,310, filed Mar. 8, 2011, entitled PHOSPHOR COMPOSITION, by Yi-Qun Li et al., which applications are incorporated herein by reference in their entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Embodiments of the present disclosure are directed to yellow-green to yellow-emitting phosphors based on aluminates that contain the rare earth terbium (Tb). Such phosphors are applicable to a number of different technologic areas, including general lighting systems, white light illumination systems based on white LEDs, signal lights, indicator lights, etc., as well as display applications such as display backlighting, plasma display panels, LED-based display panels, and the like.

2. Description of the Related Art

Embodiments of the present invention are directed to aluminate-based phosphors that, when activated by cerium, and when doped with the rare earth terbium (Tb) emit visible light in the yellow-green to yellow portion of the electromagnetic spectrum. The phosphor may also include the rare earths lutetium (Lu) and/or gadolinium (Gd). The phrase “visible light in the yellow-green to yellow portion of the electromagnetic spectrum” is defined to mean light having a peak emission wavelength of about 550 nm to about 600 nm. Such phosphors may be used in commercial markets where white light is generated using so-called “white light LEDs,” noting as an aside that this term is somewhat of a misnomer, since light emitting diodes emit light of a specific monochromatic color and not a combination of wavelengths perceived as white by the human eye. The term is nonetheless entrenched in the lexicon of the lighting industry.

Historically, YAG:Ce (yttrium aluminate garnet activated with cerium) has been used to supply the yellow component of the light in the lighting systems mentioned above. In comparison to other phosphor hosts, particularly those based on the silicates, sulphates, nitridosilicates, and oxo-nitridosilicates, YAG:Ce has a relatively high absorption efficiency

when excited by blue light, is stable in high temperature and humidity environments, and has a high quantum efficiency (QE>95%), all the while displaying a broad emission spectrum.

One disadvantage to using a YAG:Ce based phosphor, other than inadequate color rendering in some situations, is that the peak emission of this phosphor is too long, that is to say, too deep towards the orange or red for use as a luminescent source in, for example, a backlighting application. An alternative to YAG:Ce is the cerium doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ compound (LAG:Ce), which has the same crystalline structure as YAG:Ce, a similar temperature and humidity stability as the yttrium-based compound, and likewise quantum efficiency. Despite these similarities, LAG:Ce exhibits a different peak emission wavelength than its YAG counterpart; in the lutetium case, this peak wavelength is at about 540 nm. This emission wavelength is still not short enough, however, to be ideal for certain applications such as backlighting applications, and general lighting applications, where appropriate.

Thus, what is needed in the art, particularly in fields related to backlighting technologies and general lighting, is a phosphor with a structure comparable to a garnet in terms of temperature and humidity stability, but having at the same time a peak emission wavelength ranging from about 550 nm to about 600 nm. According to the present embodiments, these challenges may be addressed by providing lutetium (Lu) aluminate-based phosphors that include the rare earth terbium (Tb). The phosphors may also include the rare earth gadolinium (Gd).

SUMMARY OF THE INVENTION

Embodiments of the present disclosure are directed to yellow-green and yellow-emitting, lutetium aluminate-based phosphors containing terbium (Tb) and in some embodiments gadolinium (Gd) in addition to Tb. These phosphors may be used in white LEDs, in general lighting applications, and in LED and backlighting displays.

In one embodiment of the present invention, the phosphor may comprise a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor comprising terbium (Tb), aluminum (Al), and oxygen (O), wherein the phosphor is configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm, and to emit light having a peak emission wavelength ranging from about 550 nm to about 600 nm. The yellow-green to yellow-emitting aluminate-based phosphor may be excited by radiation having a wavelength ranging from about 420 nm to about 480 nm. The phosphor may have the formula $(\text{Lu}_{1-x}\text{Tb}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$, wherein x ranges from about 0.1 to less than 1.0, and wherein the phosphor is configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm, and to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm. The phosphor may further include the rare earth element gadolinium (Gd) and have the formula $(\text{Lu}_{1-x-y}\text{Tb}_x\text{Gd}_y)_3\text{Al}_5\text{O}_{12}:\text{Ce}$, wherein x ranges from about 0.1 to less than 1.0, y is greater than zero, and $x+y<1$. Furthermore, the Tb-containing phosphors may have a shift in CIE coordinates of less than 0.005 for both x and y coordinates over a temperature range from 20° C. to 220° C.—specific examples of such phosphors include $(\text{Lu}_{0.67}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, $(\text{Lu}_{0.47}\text{Tb}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ and $(\text{Lu}_{0.47}\text{Gd}_{0.2}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$.

In another embodiment of the present invention, the phosphor comprises a cerium-activated, yellow-green to

3

yellow-emitting aluminate-based phosphor having the formula $(\text{Lu}_{1-x}\text{A}_x\text{Ce}_y)_3\text{B}_2\text{Al}_5\text{O}_{12}\text{C}_z$; wherein A is Tb; B is at least one of Mg, Sr, Ca, and Ba; C is at least one of F, Cl, Br, and I; $0.001 \leq x \leq 1.0$; $0.001 \leq y \leq 0.2$; and $0 \leq z \leq 0.5$.

In another embodiment of the present invention, the phosphor comprises a cerium-activated, yellow-green to yellow-emitting aluminate-based phosphor represented by the formula $(\text{Lu}_{0.97-x}\text{A}_x\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. Here, A is Tb, and may further include Gd; and x ranges from about 0.001 to about 1.0.

According to further embodiments of the present invention, a white light illumination system may comprise: an excitation source with emission wavelength within a range of 200 nm to 480 nm; at least one of a red-emitting phosphor or a green-emitting phosphor; and a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor comprising terbium, wherein the phosphor is configured to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm. The cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may be configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm. The cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may further comprise gadolinium.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures, wherein:

FIG. 1 shows the SEM morphology of $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with different MgF_2 additive concentrations, illustrating that particle sizes become larger and more homogeneous as the amount of the MgF_2 additive is increased;

FIG. 2 is a series of x-ray diffraction (XRD) patterns of exemplary $\text{Y}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations;

FIG. 3 is a series x-ray diffraction (XRD) patterns of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations;

FIG. 4 is a series of the x-ray diffraction (XRD) patterns of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors having a 5 wt % MgF_2 additive and a 5 wt % SrF_2 additive;

FIG. 5 is the emission spectra of a series of exemplary $\text{Y}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different levels of MgF_2 additive, the emission spectra are obtained by exciting the phosphors with a blue LED;

FIG. 6 is the normalized emission spectra of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations under blue LED excitation;

FIG. 7 is the emission spectra of $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations under blue LED excitation;

FIG. 8 is the normalized emission spectra of $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different levels of MgF_2 additive under blue LED excitation; the results show that the emission peak of $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ shifts to shorter wavelength with a certain amount of MgF_2 additive, and that the greater the amount of the MgF_2 additive, the shorter the emission peak wavelength;

FIG. 9 is a normalized emission spectra of a $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphor with 5 wt % MgF_2 and 5 wt % SrF_2 additives where the phosphor has been excited with a

4

blue LED; the results are compared with a control sample that contains no halogenated salt additives; the results illustrate that the emission peak shifts to shorter wavelengths with the MgF_2 synthesized compound than it does for the SrF_2 synthesized compound;

FIG. 10 shows how the emission wavelength of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors decreases as the concentration of an SrF_2 additive is increased;

FIG. 11 is the normalized excitation spectra of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations, showing that the excitation spectrum becomes narrower as the MgF_2 additive concentration is increased;

FIG. 12 shows the temperature dependence of an exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphor with a 5 wt % MgF_2 additive, as compared with a commercial Ce:YAG phosphor;

FIG. 13 shows the spectra of a white LED that includes an exemplary green-emitting, aluminate-based phosphor having the formula $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with 5 wt % SrF_2 additive; the white LED also includes a red phosphor having the formula $(\text{Ca}_{0.2}\text{Sr}_{0.8})\text{AlSiN}_3:\text{Eu}^{2+}$, and when both green and red phosphors are excited with an InGaN LED emitting blue light, the resulting white light had the color properties CIE x=0.24, and CIE y=0.20;

FIG. 14 is the spectra of a white LED with the following components: a blue InGaN LED, a green garnet having the formula $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with either 3 or 5 wt % additives of MgF_2 and SrF_2 , respectively, a red nitride having the formula $(\text{Ca}_{0.2}\text{Sr}_{0.8})\text{AlSiN}_3:\text{Eu}^{2+}$ or a silicate having the formula $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{SiO}_4:\text{Eu}^{2+}$, wherein the white light has the color coordinates CIE (x=0.3, y=0.3);

FIG. 15 is the spectra of the white LED systems of FIG. 14, in this instance measured at 3,000 K;

FIGS. 16A-B shows that the peak emission wavelength of these halogenated aluminates ranged overall from about 550 nm to about 580 nm as the Gd level was increased, where the Ba level was fixed stoichiometrically at 0.15 for the Ba series, and where the Sr level was fixed stoichiometrically at 0.34;

FIGS. 17A-B are the x-ray diffraction patterns of both the Ba series and the Sr series of phosphors whose luminosity data was depicted in FIGS. 16A-B;

FIGS. 18-20 are photoemission spectra of representative Tb and/or Gd-containing phosphors excited by a blue light source, according to the present embodiments; the spectra plot photoluminescent intensity as a function of photoemission wavelength;

FIG. 21 is a plot of peak emission wavelength versus either Gd or Tb concentrations, and thus shows the effect of the amount of Gd and/or Tb inclusion on peak photoemission wavelength;

FIG. 22 is a plot of photoluminescent intensity versus peak emission wavelength for the same series of phosphors with varying Gd concentration and Tb concentration studied in FIG. 21; and

FIG. 23 is a graph of the CIE y-coordinate plotted against CIE x-coordinate for a series of exemplary phosphors being subjected to an increase in temperature; the data shows that increasing temperature leads to a decrease in the value of the CIE y-coordinate, and an increase in the CIE x-coordinate.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the present invention will now be described in detail with reference to the drawings, which are

provided as illustrative examples of the invention so as to enable those skilled in the art to practice the invention. Notably, the figures and examples below are not meant to limit the scope of the present invention to a single embodiment, but other embodiments are possible by way of interchange of some or all of the described or illustrated elements. Moreover, where certain elements of the present invention can be partially or fully implemented using known components, only those portions of such known components that are necessary for an understanding of the present invention will be described, and detailed descriptions of other portions of such known components will be omitted so as not to obscure the invention. In the present specification, an embodiment showing a singular component should not be considered limiting; rather, the invention is intended to encompass other embodiments including a plurality of the same component, and vice-versa, unless explicitly stated otherwise herein. Moreover, applicants do not intend for any term in the specification or claims to be ascribed an uncommon or special meaning unless explicitly set forth as such. Further, the present invention encompasses present and future known equivalents to the known components referred to herein by way of illustration.

A yttrium aluminum garnet compound activated with the rare earth cerium (YAG:Ce) has been, historically, one of the most common choices of phosphor material made if the desired application was either high power LED lighting, or cool white lighting of a non-specific, general nature. As one might expect, there is a requirement in general lighting for highly efficient components, both in the case of the LED chip supplying the blue light component of the resultant white light, and the excitation radiation for the phosphor, where the phosphor typically supplies the yellow/green constituent of the resulting product white light.

As discussed in the previous section of this disclosure, YAG:Ce demonstrates this desired high efficiency, having a quantum efficiency greater than about 95 percent, and it would therefore appear to be a difficult task to improve upon this number. But it is known in the art that the efficiency of an LED chip increases with a decrease in emission wavelength, and thus it would appear, in theory anyway, that the efficiency of a general lighting system will be enhanced if a phosphor paired with an LED chip emitting at shorter wavelengths may be excited by those shorter wavelengths. The problem with this strategy, unfortunately, is that the emission efficiency of a YAG:Ce phosphor decreases when the wavelength of its blue excitation radiation is reduced to a level below about 460 nm.

The repercussions of this are, of course, that YAG:Ce should really only be paired with an LED chip having an emission wavelength no less than about 450 to 460 nm. But it is also known in the art that photon energies of the phosphor's excitation radiation depend strongly on the structure of the anionic polyhedron (comprising oxygen atoms in this case) surrounding the activator cation (cerium). It follows that the efficiency of the system may be enhanced if the excitation range of a garnet-based phosphor might be extended towards shorter wavelengths relative to a YAG:Ce phosphor. Thus, one of the objects of the present invention include altering the structure and nature of this anionic polyhedron to shift the excitation range the phosphor "desires" to see to shorter wavelengths relative to that of the traditional YAG:Ce, while maintaining in the meantime (or even improving) the enhanced properties that many garnets display.

The present disclosure will be divided into the following sections: first, a chemical description (using stoichiometric

formulas) of the present halogenated aluminates will be given, followed by a brief description of viable synthetic methods that may be used to produce them. The structure of the present halogenated aluminates will be discussed next, along with its relationship to experimental data comprising wavelength and photoluminescent changes upon the inclusion of certain halogen dopants. Finally, the role these yellow-green and yellow-emitting phosphors may play in white light illumination, general lighting, and backlighting applications will be presented with exemplary data.

Chemical Description of the Present Halogenated Aluminate-Based Phosphors

The yellow to green-emitting, aluminate-based phosphors of the present invention contain both alkaline earth and halogen constituents. These dopants are used to achieve the desired photoemission intensity and spectral properties, but the fact that simultaneous alkaline earth and halogen substitutions provide a sort of self-contained charge balance is fortuitous as well. Additionally, there may be other advantageous compensations having to do with the overall changes to the size of the unit cell: while substitutions of any of Sc, La, Gd, and/or Tb for Lu (either individually, or in combinations) may tend to expand or contract the size of the cell, the opposite effect may occur with substitutions of halogen for oxygen.

There are several ways to describe the formula of the present phosphors. In one embodiment, a green emitting, cerium-doped, aluminate-based phosphor may be described by the formula $(\text{Lu}_{1-a-b-c}\text{Y}_a\text{M}_b\text{A}_c)_3(\text{Al}_{1-d}\text{B}_d)_5(\text{O}_{1-e}\text{C}_e)_{12}:\text{Ce}$, Eu, where A is selected from the group consisting of Mg, Sr, Ca, and Ba; B is selected from the group consisting of Ga and In; C is selected from the group consisting of F, Cl, and Br; $0 \leq a \leq 1$; $0 \leq b \leq 1$; $0 < c \leq 0.5$; $0 < d \leq 1$; and $0 < e \leq 0.2$. The "A" element, which may be any of the alkaline earth elements Mg, Sr, Ca, and Ba, used either solely or in combination, is very effective in shifting emission wavelength to shorter values. These compounds will be referred to in the present disclosure as "halogenated LAG-based" aluminates, or simply "halogenated aluminates."

In an alternative embodiment, the present yellow to green-emitting, aluminate-based phosphors may be described by the formula $(\text{Y,A})_3(\text{Al,B})_5(\text{O,C})_{12}:\text{Ce}^{3+}$, where A is at least one of Tb, Gd, Sm, La, Lu, Sr, Ca, and Mg, including combinations of those elements, wherein the amount of substitution of those elements for Y ranges from about 0.1 to about 100 percent in a stoichiometric manner. B is at least one of Si, Ge, B, P, and Ga, including combinations, and these elements substitute for Al in amounts ranging from about 0.1 to about 100 percent stoichiometrically. C is at least one of F, Cl, N, and S, including combinations, substituting for oxygen in amounts ranging from about 0.1 to about 100 percent stoichiometrically.

In an alternative embodiment, the present yellow to green-emitting, aluminate-based phosphors may be described by the formula $(\text{Y}_{1-x}\text{Ba}_x)_3\text{Al}_5(\text{O}_{1-y}\text{C}_y)_{12}:\text{Ce}^{3+}$, where x and y each range from about 0.001 to about 0.2.

In an alternative embodiment, a yellow-green to green-emitting, aluminate-based phosphor may be described by the formula $(\text{A}_{1-x}\text{B}_x^{3+}\text{B}_x^{2+})_m\text{Al}_5(\text{O}_{1-y}^{2-}\text{C}_y^{1-})_n:\text{Ce}^{3+}$, where A is selected from the group consisting of Y, Sc, Gd, Tb, and Lu; B is selected from the group consisting of Mg, Sr, Ca, and Ba; C is selected from the group consisting of F, Cl, and Br; $0 \leq x \leq 0.5$; $0 < y \leq 0.5$; $2 \leq m \leq 4$; and $10 \leq n \leq 14$.

In an alternative embodiment, a yellow-green to green-emitting, aluminate-based phosphor may be described by the formula $(\text{A}_{1-x}\text{B}_x^{3+}\text{B}_x^{2+})_m\text{Al}_5(\text{O}_{1-y}^{2-}\text{C}_y^{1-})_n:\text{Ce}^{3+}$, where A is

selected from the group consisting of Y, Sc, Gd, Tb, and Lu; B is selected from the group consisting of Mg, Sr, Ca, and Ba; C is selected from the group consisting of F, Cl, and Br; $0 \leq x \leq 0.5$; $0 \leq y \leq 0.5$; $2 \leq m \leq 4$; and $10 \leq n \leq 14$; subject to the proviso that m is not equal to 3.

In an alternative embodiment, a yellow-green to green-emitting, aluminate-based phosphor may be described by the formula $(A_{1-x}B_x)_{m'}Al_5(O_{1-y}C_y)_{n'}Ce^{3+}$, where A is selected from the group consisting of Y, Sc, Gd, Tb, and Lu; B is selected from the group consisting of Mg, Sr, Ca, and Ba; C is selected from the group consisting of F, Cl, and Br; $0 \leq x \leq 0.5$; $0 \leq y \leq 0.5$; $2 \leq m \leq 4$; and $10 \leq n \leq 14$; subject to the proviso that n is not equal to 12.

In an alternative embodiment, a yellow to green-emitting, aluminate-based phosphor may be described by the formula $(Lu_{1-x-y}A_xCe_y)_3B_zAl_5O_{12}C_{2z}$, where A is at least one of Sc, La, Gd, and Tb; B is at least one of the alkaline earths Mg, Sr, Ca, and Ba; C is at least one of the halogen elements F, Cl, Br, and I; and the values of the parameters x, y, z are $0 \leq x \leq 0.5$; $0.001 \leq y \leq 0.2$; and $0.001 \leq z \leq 0.5$. It is noted that "at least one of" with regard to the formulas in this disclosure means that the elements in that group may appear in the phosphor either individually, or in combinations, where any combinations of any of the elements in that group are allowable, provided that the total amount of that group satisfies the rule assigned to it in terms of overall stoichiometric amounts.

One of ordinary skill in the art will appreciate that the relationship between the amounts of C, the halogen, and B, the alkaline earth, may not always be present in the phosphor product at the expected ratio of 2:1 (stoichiometrically speaking) after a processing step such as sintering if the C and B components are added to the starting mix of materials in the form of an alkaline earth salt (e.g., $B^{2+}C_2$). This is because the halogen component is known to be volatile, and in some instances, some of the C is lost relative to B such that the ratio of B to C in the final phosphor product is less than 2:1. Thus, in an alternative embodiment of the present invention, the amount of C is less than 2z in the formula by an amount of up to 5 percent by number. In various other embodiments, the amount of C is less than 2z by an amount of up to 10, 25, and 50 percent stoichiometrically.

Synthesis

Any number of methods may be used to synthesize the present yellow-green to yellow-emitting, aluminate-based phosphors, methods that may involve both solid state reaction mechanisms as well as liquid mixing techniques. Liquid mixing includes such methods as co-precipitation and sol-gel techniques.

One embodiment of preparation involves a solid state reaction mechanism comprising the steps:

- (a) desired amounts of the starting materials CeO_2 , Y_2O_3 , lutetium salts including the nitrates, carbonates, halides, and/or oxides of lutetium, salts of the other rare earths Sc, La, Gd, and Tb, and $M^{2+}X_2$, where M is a divalent alkaline earth metal selected from the group consisting of Mg, Sr, Ca, and Ba, and X is a halogen selected from the group consisting of F, Cl, Br, and I were combined to form a mixture of starting powders;
- (b) the mix of starting powders from step (a) is dry-mixed using any conventional method, such as ball milling, and typical mixing times using ball milling are greater than about 2 hours (in one embodiment about 8 hours);
- (c) sintering the mixed starting powders from step (b) at a temperature of about 1400° C. to about 1600° C. for about 6 to about 12 hours in a reducing atmosphere (the

purpose of this atmosphere is for a reduction of the ammonia-based compounds);

- (d) crushing the sintered product from step (c), and washing it with water; and

- (e) drying the washed product from step (d), wherein the drying conditions may be constitute a time of about 12 hours at a temperature of about 150° C.

The present aluminates may be synthesized by liquid mixing techniques. An example of the synthesis of a non-halogenated LAG compound having the formula $Lu_{2.985}Ce_{0.015}Al_5O_{12}$ using co-precipitation has been described by H.-L. Li et al. in an article titled "Fabrication of Transparent Cerium-Doped Lutetium Aluminum Garnet Ceramics by Co-Precipitation Routes," *J. Am. Ceram. Soc.* 89 [7] 2356-2358 (2006). These non-halogenated LAG compounds contained no alkaline earth constituents. The article is incorporated herein in its entirety, as it is contemplated that a similar co-precipitation method may be used to produce the halogenated LAGs of the present disclosure with alkaline earth constituents.

An example of the synthesis of a halogenated YAG compound using a sol-gel technique has been described in U.S. Pat. No. 6,013,199 by E. McFarland et al., to Symyx Technologies, titled "Phosphor materials." These (possibly) halogenated YAG compounds contained no alkaline earth constituents. This patent is incorporated herein in its entirety, as it is contemplated that a similar sol-gel method may be used to produce the halogenated YAG compounds of the present disclosure with alkaline earth constituents.

FIG. 1 shows the SEM morphology of an exemplary $Lu_{2.91}Ce_{0.09}Al_5O_{12}$ phosphors with different MgF_2 additive concentrations, synthesized via the solid state mechanisms described above. The morphology as revealed by scanning electron microscope (SEM) shows that particle sizes become larger, and more homogeneous, as the amount of the MgF_2 additive is increased. The phosphor particles are roughly 10 to 15 microns in diameter.

Crystal Structure of the Present Yellow-Green to Yellow Emitting Aluminates

The crystal structure of the present yellow-green to yellow aluminates is similar to that of the yttrium aluminum garnet, $Y_3Al_5O_{12}$, and in keeping with this well studied YAG compound, the present aluminates may belong to the space group Ia3d (no. 230). This space group, as it pertains to YAG, has been discussed by Y. Kuru et al. in an article titled "Yttrium Aluminum Garnet as a Scavenger for Ca and Si," *J. Am. Ceram. Soc.* 91 [11] 3663-3667 (2008). As described by Y. Kuru et al., YAG has a complex crystal consisting of 160 atoms (8 formula units) per unit cell, where the Y^{3+} occupy positions of multiplicity 24, Wyckoff letter "c," and site symmetry 2.22, and the O^{2-} atoms occupy positions of multiplicity 96, Wyckoff letter "h," and site symmetry 1. Two of the Al^{3+} ions are situated on octahedral 16(a) positions, whereas the remaining three Al^{3+} ions are positioned on tetrahedral 24(d) sites.

The lattice parameters of the YAG unit cell are $a=b=c=1.2008$ nm, and $\alpha=\beta=\gamma=90^\circ$. Whereas substitution of lutetium for yttrium is expected to expand the size of the unit cell, the angles between the unit cell axes are not expected to change, and the material will retain its cubic character.

FIG. 2 shows the x-ray diffraction (XRD) patterns of a series of exemplary $Y_{2.91}Ce_{0.09}Al_5O_{12}$ phosphors with different MgF_2 additive concentrations, showing how the addition of an alkaline earth and a halogen (MgF_2) component shifts high angle diffraction peaks to higher values of 2θ . This means that the lattice constants become smaller relative to a YAG component with no alkaline earth/halogen, and

further indicates that Mg^{2+} is being incorporated into the crystal lattice, occupying Y^{3+} positions.

FIG. 3 shows the x-ray diffraction (XRD) pattern of a series of exemplary phosphors in an analogous manner to FIG. 2, except that this time the series of compounds are $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations, where lutetium-based compounds are being studied, rather than yttrium-based compounds.

FIG. 4 shows the x-ray diffraction (XRD) pattern of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors having either a 5 wt % MgF_2 and 5 wt % SrF_2 additive; this experiment shows a comparison of the Mg constituent versus an Sr constituent. The data shows that with the MgF_2 additive in the $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ lattice, high angle diffraction peak move to greater values of 2θ , meaning that lattice constants become smaller. Alternatively, with SrF_2 additive, high angle diffraction peaks move to smaller values of 2θ , meaning that the lattice constants increase. It will be apparent to those skilled in the art that both Mg^{2+} and Sr^{2+} are being incorporated into the $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ lattice and occupying Lu^{3+} positions. These peak shifts in position occur because Mg^{2+} , with its ionic radius of 0.72 Å, is smaller than Lu^{3+} (0.86 Å), while Sr^{2+} (1.18 Å) is bigger than Lu^{3+} .

Mechanism of Alkaline Earth and Halogen Influence on Optical Properties

In one embodiment of the present invention, Ce^{3+} is the luminescent activator in the aluminate-based phosphor. The transition between the 4f and 5d energy levels of the Ce^{3+} ion corresponds to excitation of the phosphor with blue light; green light emission from the phosphor is a result from the same electronic transition. In the aluminate structure, the Ce^{3+} is located at the center of an octahedral site formed by a polyanionic structure of six oxygen ions. It will be appreciated by those skilled in the art that according to crystal field theory, the surrounding anions (which may also be described as ligands) induce an electrostatic potential on the 5d electron of the central cation. The 5d energy level splitting is 10Dq, where Dq is known to depend on the particular ligand species. From the spectrochemical series it may be seen that the Dq of a halide is smaller than that of oxygen, and thus it follows that when oxygen ions are replaced by halide ions, the Dq will decrease correspondingly.

The implications of this are that the band gap energy; that is to say, the energy difference between the 4f and 5d electronic levels, will increase with substitution of oxygen ions with halide in the polyanionic cages surrounding activator ions. This is why the emission peak shifts to shorter wavelength with halogen substitution. Simultaneously, with the introduction of halide ions in the oxygen polyanionic structures forming octahedral sites, a corresponding cation may also replace a portion of the Lu (and/or Sc, La, Gd, and Tb) content. If the cation replacing Lu (and/or the other rare earths) is a smaller cation, the result will be a shift of the emission peak towards the blue end of the spectrum. The emitted luminescence will have a shorter wavelength than otherwise would have occurred. In contrast, if the cation replacing Lu is a larger cation, such as Sr or Ba, the result will be a shift of the emission peak towards the red end of the spectrum. In this case, the emitted luminescence will have a longer wavelength.

Combined with the effects of the halide, Mg as an alkaline earth substituent will be a better choice than Sr if a blue-shift is desired, and this will be shown experimentally in the following portions of the present disclosure. It is also known the LAG emission peak is a doublet due to spin-orbit

coupling. As the blue-shift occurs, the emission with shorter wavelength is biased and its intensity increases correspondingly. This trend is not only helpful to the blue-shift of the emission, but also enhances photoluminescence.

FIG. 5 is the emission spectra of a series of exemplary $\text{Y}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different levels of MgF_2 additive, the emission spectra obtained by exciting the phosphors with a blue LED. This data shows that with increasing amounts of MgF_2 the photoluminescent intensity increases and the peak emission wavelength shifts to shorter values. Though not shown on FIG. 5, the present inventors have data for a 5 wt % addition of BaF_2 to the starting powders: this phosphor showed a significant increase in photoluminescent intensity relative to the three magnesium-containing phosphors, and a peak emission wavelength that the same about as that of the 1 wt % sample.

A normalized version of the data from FIG. 5 is shown in FIG. 6. FIG. 6 is the normalized emission spectra of the same series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations under blue LED excitation, but where normalizing the photoluminescent intensity to a single value highlight that the emission peak of $\text{Y}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ shifts to short wavelength with increasing amounts of the MgF_2 additive. The greater the amount of the MgF_2 additive, the shorter emission peak wavelength. This is the same trend with demonstrated by a $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphor, as will be demonstrated next.

FIG. 7 is the emission spectra of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different levels of MgF_2 additive, the emission spectra obtained by exciting the phosphor with a blue LED. This data is analogous to that of FIG. 5, except that lutetium-based rather than yttrium-based compounds are being studied. As with the yttrium data, this data for lutetium shows similar trends for the shift in emission wavelength, though those trends for photoluminescent intensity are not, perhaps, as similar.

The $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ emission spectra of FIG. 7 has been normalized to emphasize the effect of the addition of halogen salt on peak emission wavelength; the normalized version of the data is shown in FIG. 8. As in the yttrium case, peak emission shifts to shorter wavelength with increasing amounts of MgF_2 additive; that is to say, the greater the amount of the MgF_2 additive, the shorter emission peak wavelength. The amount of wavelength shift upon increasing the amount of the MgF_2 additive from zero (no additive) to about 5 wt % of the additive was observed to be about 40 nm; from about 550 nm to about 510 nm.

Each of the graphs in FIGS. 5-8 have plotted their respective spectra as a series of phosphor compositions with increasing additive concentration, starting at no additive, and ending with the highest concentration of the series at 5 wt %. To emphasize a comparison of the SrF_2 additive with the MgF_2 additive; in other words, a phosphor with an Sr alkaline earth and fluorine content with a phosphor having a Mg alkaline earth and fluorine content, the phosphors have been plotted together in FIG. 9: a phosphor with no additive, a phosphor with 5 wt % SrF_2 , and a phosphor with 5 wt % MgF_2 . The phosphor is based on the sample $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$.

The emission spectra data in FIG. 9 has been normalized to better emphasize the effects on optical properties rendered by the inclusion the halogen and alkaline earths. When excited with a blue LED, the result illustrates that the emission peak shift to shorter wavelengths with the addition of MgF_2 and SrF_2 . The $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ sample with no additive shows a peak emission wavelength at about 550 nm; with a 5 wt % SrF_2 additive the peak emission wave-

length shifts to about 535 nm, and with a 5 wt % MgF_2 additive the wavelength shifts even further to about 510 nm.

FIG. 10 shows how the emission wavelength of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors decreases as the concentration of an SrF_2 additive is increased. Peak emission wavelength has been plotted as a function of the amount of the SrF_2 additive; samples having an SrF_2 additive content of 1, 2, 3, and 5 wt % were tested. The results show that the peak emission wavelength was about the same for the 1 and 2 wt % samples, the wavelength being about 535 nm; as the SrF_2 additive is increased to 3 wt % the peak emission wavelength decreases to about 533 nm. With a further increase of SrF_2 additive to 5 wt % peak wavelength drops precipitously to about 524 nm.

Excitation Spectra and Temperature Dependence

FIG. 11 is the normalized excitation spectra of a series of exemplary $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ phosphors with different MgF_2 additive concentrations, showing that the excitation spectra becomes more narrow when the MgF_2 additive concentration is increased. The data shows that the present green emitting, aluminate-based phosphors exhibit a wide band of wavelengths over which the phosphors may be excited, ranging from about 380 to about 480 nm.

The thermal stability of the present garnet phosphors is exemplified by the lutetium containing compound $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with a 5 wt % MgF_2 additive; its thermal stability is compared with the commercially available phosphor $\text{Ce}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ in FIG. 12. It may be observed that the thermal stability of the $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ compound is even better than the YAG.

Applications to Backlighting and White Light Illumination Systems

According to further embodiments of the present invention, the present green emitting, aluminate-based phosphors may be used in white light illumination systems, commonly known as "white LEDs," and in backlighting configurations for display applications. Such white light illumination systems comprise a radiation source configured to emit radiation having a wavelength greater than about 280 nm; and a halide anion-doped green aluminate phosphor configured to absorb at least a portion of the radiation from the radiation source, and emit light having a peak wavelength ranging from 480 nm to about 650 nm.

FIG. 13 shows the spectra of a white LED that includes an exemplary green-emitting, aluminate-based phosphor having the formula $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with a 5 wt % SrF_2 additive. This white LED further includes a red phosphor having the formula $(\text{Ca}_{0.2}\text{Sr}_{0.8})\text{AlSiN}_3:\text{Eu}^{2+}$. When both green aluminate and red nitride phosphors are excited with an InGaN LED emitting blue light, the resulting white light displayed the color coordinates CIE $x=0.24$, and CIE $y=0.20$.

FIG. 14 is the spectra of a white LED with the following components: a blue InGaN LED, a green garnet having the formula $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with either 3 or 5 wt % additives, a red nitride having the formula $(\text{Ca}_{0.2}\text{Sr}_{0.8})\text{AlSiN}_3:\text{Eu}^{2+}$ or a silicate having the formula $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{SiO}_4:\text{Eu}^{2+}$, wherein the white light has the color coordinates CIE ($x=0.3$, $y=0.3$). The sample that shows the most prominent double peak is the one labeled "EG3261+R640," where the EG3261 designation represents the $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor, in combination with the red R640 $(\text{Ca}_{0.2}\text{Sr}_{0.8})\text{AlSiN}_3:\text{Eu}^{2+}$ phosphor emitting at about 640 nm. The two peaks labeled LAG (3 wt % MgF_2)+R640 and LAG (5 wt % SrF_2)+R640 demonstrate a much more uniform emission of perceived white light over the wavelength range 500 to 650 nm, an attribute desirable in the art.

FIG. 15 is the spectra of the white LED systems of FIG. 14, in this instance measured at 3,000 K.

In embodiments of the present invention, the red nitride that may be used in conjunction with the green aluminate may have the general formula $(\text{Ca},\text{Sr})\text{AlSiN}_3:\text{Eu}^{2+}$, where the red nitride may further comprise an optional halogen, and wherein the oxygen impurity content of the red nitride phosphor may be less than equal to about 2 percent by weight. The yellow-green silicates may have the general formula $(\text{Mg},\text{Sr},\text{Ca},\text{Ba})_2\text{SiO}_4:\text{Eu}^{2+}$, where the alkaline earths may appear in the compound either individually, or in any combination, and wherein the phosphor may be halogenated by F, Cl, Br, or I (again, either individually, or in any combination).

Optical and Physical Data in Table Form

A summary of exemplary data is tabulated in Tables 1 & 2. In Table 1 is the testing results of a $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ based phosphor with three different MgF_2 additive levels. Table 2 tabulates the testing results of a $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ based compound with four different SrF_2 additive. These results summarize and confirm that MgF_2 and SrF_2 additives in $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ shift the emission peak wavelength to shorter wavelengths, where the emission intensity is increased with increasing MgF_2 and SrF_2 concentration. The particle size also increases with the increasing MgF_2 and SrF_2 additive concentration.

TABLE 1

Testing results of $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with different MgF_2 levels of additive

MgF_2 (wt %)	CIE x	CIE y	Emission Peak Wavelength (nm)	Relative Intensity (%)	Particle Size D50 (μm)
1	0.3635	0.5862	526.88	58.04	4.01
2	0.3554	0.5778	529.56	78.47	7.38
3	0.3336	0.5776	514.22	105.13	9.30

TABLE 2

Testing results of $\text{Lu}_{2.91}\text{Ce}_{0.09}\text{Al}_5\text{O}_{12}$ with different levels of SrF_2 additive

SrF_2 (wt %)	CIE x	CIE y	Emission Peak Wavelength (nm)	Relative Intensity (%)	Particle Size D50 (μm)
1	0.3677	0.5732	534.64	71.65	3.84
2	0.3677	0.5732	534.64	85.82	5.24
3	0.3555	0.5718	532.43	112.40	9.90
5	0.3405	0.5748	523.44	107.67	11.38

Yellow-Green to Yellow Emitting, Rare Earth Doped Aluminate-Based Phosphors

The rare earth doping of a specific series of yellow-green to yellow emitting, halogenated aluminates were tested by the present inventors, where the phosphors had the general formula $(\text{Lu}_{1-x-y}\text{A}_x\text{Ce}_y)_3\text{B}_z\text{Al}_5\text{O}_{12}\text{C}_{2-z}$. As disclosed above, A is at least one of Sc, La, Gd, and Tb; B is at least one of the alkaline earths Mg, Sr, Ca, and Ba; C is at least one of the halogen elements F, Cl, Br, and I; and the values of the parameters x, y, z are $0 \leq x \leq 0.5$; $0.001 \leq y \leq 0.2$; and $0.001 \leq z \leq 0.5$. In this series of phosphors, the rare earth dopant was Gd, and the alkaline earth was either Ba or Sr. The halogen was F in all of the compounds tested in this series of experiments. The formulas of the specific aluminates tested are shown in Table 3.

TABLE 3

Testing results of $(\text{Lu}_{1-x-y}\text{Gd}_x\text{Ce}_y)_3\text{B}_z\text{Al}_5\text{O}_{12}\text{F}_{2z}$ with B = Ba and B = Sr for different values of x, y and z				
Composition	CIE x CIE y	Emission Peak Wavelength (nm)	Relative PL Intensity (%)	Particle Size D50 (μm)
$(\text{Lu}_{0.90}\text{Gd}_{0.07}\text{Ce}_{0.03})_3\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.30}$	0.424 0.543	554	114	12.02
$(\text{Lu}_{0.80}\text{Gd}_{0.17}\text{Ce}_{0.03})_3\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.30}$	0.453 0.525	565	111	11.15
$(\text{Lu}_{0.64}\text{Gd}_{0.33}\text{Ce}_{0.03})_3\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.30}$	0.480 0.505	576	101	9.59
$(\text{Lu}_{0.94}\text{Gd}_{0.03}\text{Ce}_{0.03})_3\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$	0.413 0.550	551	132	15.61
$(\text{Lu}_{0.90}\text{Gd}_{0.07}\text{Ce}_{0.03})_3\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$	0.429 0.545	555	138	12.94
$(\text{Lu}_{0.84}\text{Gd}_{0.13}\text{Ce}_{0.03})_3\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$	0.436 0.537	558	122	14.44

For the purpose of this disclosure, a green emission will be defined as having a peak emission wavelength of from about 500 nm to about 550 nm. Emissions extending from about 550 nm to about 600 nm may be described as containing wavelengths that change from a yellow-green color to a yellow color. The addition of Gd doping converts the phosphor from a substantially green-emitting sample to a substantially yellow sample in the experiments described; though not shown, increasing the Gd concentration even further (from about 0.33 for Ba samples and from about 0.13 for Sr samples) shifts the emission further towards and into the yellow region of the electromagnetic spectrum. Making generalizations can be difficult because the peak emission wavelength depends not only on the choice and level, of the rare earth(s) dopants present in addition to lutetium (e.g., Gd in addition to Lu), but also on the selection and amounts of the included alkaline earth(s) and the halogen(s). The halogenated aluminates in the present disclosure are defined to emit in the yellow-green to the yellow region of the electromagnetic spectrum, at wavelengths from about 550 nm to about 600 nm. Green-emitting halogenated aluminates emit at peak wavelengths ranging substantially from about 500 nm to about 550 nm. For green-emitting aluminates, see U.S. patent application Ser. No. 13/181,226 filed Jul. 12, 2011, assigned to the same assignee as the present application, and hereby incorporated herein in its entirety.

The data in Table 3 and FIGS. 16A-B shows that the peak emission wavelength of these halogenated aluminates ranged overall from about 550 nm to about 580 nm as the Gd level was increased, where the Ba level was fixed stoichiometrically at 0.15 for the Ba series, and where the Sr level was fixed stoichiometrically at 0.34 for the Sr series (the concentration is stoichiometric, meaning by number, not by weight). The Ce activator level was also fixed stoichiometrically at 0.03 for all of the samples. Specifically, for the Ba samples, the peak emission wavelength increased from 554 nm to 565 nm to 576 nm as the Gd amount was increased stoichiometrically from 0.07 to 0.17 to 0.33, respectively. For the Sr samples, the peak emission wavelength increased from 551 nm to 555 nm to 558 nm as the Gd amount was increased stoichiometrically from 0.03 to 0.07 to 0.13, respectively.

The actual compounds in the Ba series were, respectively, $(\text{Lu}_{0.90}\text{Gd}_{0.07}\text{Ce}_{0.03})_3\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.30}$, $(\text{Lu}_{0.80}\text{Gd}_{0.17}\text{Ce}_{0.03})_3\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.30}$, and $(\text{Lu}_{0.64}\text{Gd}_{0.33}\text{Ce}_{0.03})_3\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.30}$. The actual compounds tested in the Sr series were, respectively, $(\text{Lu}_{0.94}\text{Gd}_{0.03}\text{Ce}_{0.03})_3\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$, $(\text{Lu}_{0.90}\text{Gd}_{0.07}\text{Ce}_{0.03})_3\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$, and $(\text{Lu}_{0.84}\text{Gd}_{0.13}\text{Ce}_{0.03})_3\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$.

It is noted that the Sr series emitted at a higher relative photoluminescent intensity when compared to the Ba series,

but one skilled in the art will know to draw conclusions carefully, as several other variables were changed at the same time (e.g., Gd content, alkaline earth amounts, and halogen concentrations).

Shown in FIGS. 17A-B are the x-ray diffraction patterns of both the Ba series and the Sr series of phosphors whose luminosity data was depicted in FIGS. 16A-B.

Yellow-Emitting, Aluminate-Based Phosphors Featuring Terbium (Tb) and/or Gadolinium (Gd).

In certain compositions, according to the present embodiments, the yellow-green to yellow emitting halogenated aluminates featured the rare earth element terbium (Tb). The present inventors have conducted experiments comparing the relative effects of terbium and gadolinium in the composition $(\text{Lu}_{0.97-x}\text{A}_x\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, where A represents at least one of Gd and Tb, either individually, or in combinations. Terbium is adjacent to gadolinium in the periodic table: the former (Tb) has atomic number 65, and electronic structure $[\text{Xe}]4f^76s^2$, whereas the latter (Gd) has atomic number 64, and electronic structure $[\text{Xe}]4f^75d6s^2$. The formula $(\text{Lu}_{0.97-x}\text{A}_x\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ shows that both terbium and gadolinium substitute for the rare earth lutetium (Lu), atomic number 71, electronic structure $[\text{Xe}]4f^{14}5d6s^2$.

Further to the methods described above for fabricating the aluminate-based phosphors, the following methods may also be used. Methods of fabricating the novel aluminate-based phosphors disclosed herein are not limited to anyone fabrication method, but may, for example, be synthesized in a three step process that includes: 1) blending starting materials, 2) firing the starting material mix, and 3) various processes to be performed on the fired material, including pulverizing and drying. In some embodiments, the starting materials may comprise various kinds of powders, such as alkaline earth metal compounds, aluminum compounds and lutetium compounds. Examples of alkaline earth metal compounds include alkaline earth metal carbonates, nitrates, hydroxides, oxides, oxalates, halides, etc. Examples of aluminum-containing compounds include nitrates, fluorides and oxides. Examples of lutetium compounds include lutetium oxide, lutetium fluoride, and lutetium chloride. The starting materials are blended in a manner such that the desired final composition is achieved. In some embodiments, the alkaline-earth, aluminum-containing compounds and lutetium compounds are blended in the appropriate ratios, and then fired to achieve the desired composition. The blended starting materials may be fired in a second step, and a flux may be used to enhance the reactivity of the blended materials (at any or various stages of the firing). The flux may comprise various kinds of halides and boron compounds, examples of which include strontium fluoride, barium fluoride, strontium chloride, barium chloride and combinations thereof. Examples of boron-containing flux

15

compounds include boric acid, boric oxide, strontium borate, barium borate and calcium borate.

In some embodiments, the flux compound is used in amounts where the number of mole percent ranges from between about 0.01 to 0.2 mole percent, where values may typically range from about 0.01 to 0.1 mole percent, both inclusive.

Various techniques for mixing the starting materials (with or without the flux) include, but are not limited to, using a mortar, mixing with a ball mill, mixing using a V-shaped mixer, mixing using a cross rotary mixer, mixing using a jet mill and mixing using an agitator. The starting materials may be either dry mixed or wet mixed, where dry mixing refers to mixing without using a solvent. Solvents that may be used in a wet mixing process include water or an organic solvent, where the organic solvent may be either methanol or ethanol. The mix of starting materials may be fired by numerous techniques known in the art. A heater such as an electric furnace or gas furnace may be used for the firing. The heater is not limited to any particular type, as long as the starting material mix is fired at the desired temperature for the desired length of time. In some embodiments, firing temperatures may range from about 800 to 1600° C. In other embodiments, the firing time may range from about 10 minutes to 1000 hours. The firing atmosphere may be selected from among air, a low pressure atmosphere, a vacuum, an inert-gas atmosphere, a nitrogen atmosphere, an oxygen atmosphere and an oxidizing atmosphere. In some embodiments, the compositions may be fired in a reducing atmosphere at between about 100° C. to about 1600° C. for between about 2 and about 10 hours. The phosphors disclosed herein may be prepared using a sol-gel method or a solid reaction method. In some embodiments, metal nitrates are used to provide the divalent metal component of the phosphor, as well as the aluminum component of the aluminate-based phosphor. In some embodiments, the metal nitrate that supplies the divalent metal component may be $\text{Ba}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ or $\text{Sr}(\text{NO}_3)_2$ and the metal nitrate that provides the aluminum may be $\text{Al}(\text{NO}_3)_3$.

This method may further include the step of using a metal oxide to provide the oxygen component of the aluminate-based phosphor. An example of the method includes the following steps: a) providing raw materials selected from the group consisting of $\text{Ba}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and Lu_2O_3 ; b) dissolving the Lu_2O_3 in a nitric acid solution and then mixing a desired amount of the metal nitrates to form an aqueous-based nitrate solution; c) heating the solution of step b) to form a gel; d) heating the gel of step c) to between about 500° C. and about 1000° C. to decompose the nitrate mixture to an oxide mixture; and e) sintering the powder of step d) in a reducing atmosphere at a temperature of between about 1000° C. and about 1500° C.

TABLE 4

Yellow-emitting, aluminate-based phosphors featuring terbium (Tb) and/or gadolinium (Gd)						
Sample No.	Gd	Tb	Ce	CIE X	CIE Y	Emission Wavelength (nm) PL (%)
T1	0	0.3	0.09	0.415	0.549	550.1 135.6
T2	0	0.5	0.09	0.433	0.539	555.8 132.5
TG1	0.2	0.3	0.09	0.442	0.534	558.4 128.3
G1	0.2	0	0.09	0.413	0.550	550 131
G2	0.3	0	0.09	0.436	0.537	556 125

16

TABLE 4-continued

Yellow-emitting, aluminate-based phosphors featuring terbium (Tb) and/or gadolinium (Gd)						
Sample No.	Gd	Tb	Ce	CIE X	CIE Y	Emission Wavelength (nm) PL (%)
G3	0.5	0	0.09	0.448	0.530	560 121
YAG1	0	0	0.09	0.427	0.548	550 140
YAG2	0	0	0.09	0.442	0.537	557 135

TABLE 5

Gd Concentration					
Gd concentration	CIE _x	CIE _y	Emi/nm	Rel. PL	D50/μm
0	0.375	0.564	541.2	140	12.8
0.1	0.394	0.556	545.4	135	13.2
0.2	0.418	0.547	551.0	130	13.0
0.3	0.434	0.538	556.1	127	13.0
0.4	0.445	0.532	559.2	125	13.5
0.5	0.452	0.528	562.8	121	13.3

TABLE 6

Tb Concentrations					
Tb concentration	CIE _x	CIE _y	Emi/nm	Rel. PL	D50/μm
0	0.375	0.564	541.2	140	12.8
0.1	0.384	0.563	542.4	138	14.0
0.3	0.415	0.549	550.1	136	13.4
0.4	0.424	0.545	552.3	134	13.6
0.5	0.430	0.541	554.8	132	13.8
0.6	0.436	0.539	556.4	131	13.5
0.75	0.444	0.533	558.3	130	13.4
0.9	0.449	0.530	560.1	129	13.0
1.0	0.453	0.528	562.0	125	13.0

Referring to Table 4, those skilled in the art will recognize that all the compositions tabulated emitted light at a peak emission wavelength ranging from about 550 nm to about 560 nm. The first two entries, labeled T1 and T2, each contain no Gd, and have Tb concentrations of $x=0.3$ and 0.5 , respectively. Thus their compositions are $(\text{Lu}_{0.67}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ and $(\text{Lu}_{0.47}\text{Tb}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, respectively. They emit with the highest relative photoluminescent intensities of the compounds in Table 4, excepting YAG1 and YAG2.

The third composition from the top in Table 4 contains both Gd and Tb in concentrations of 0.2 and 0.3 , respectively, and thus its stoichiometry is $(\text{Lu}_{0.47}\text{Gd}_{0.2}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. This compound, with the designation TG1, emitted with a peak emission wavelength that was almost as high as $(\text{Lu}_{0.47}\text{Tb}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ (555.4 nm versus 555.8 nm, respectively), although its photoluminescent intensity was not as high as either of the two compounds containing Tb only and no Gd. The latter two compounds, $(\text{Lu}_{0.67}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ and $(\text{Lu}_{0.47}\text{Tb}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, displayed a chromaticity coordinate CIE x and that was less than $(\text{Lu}_{0.47}\text{Gd}_{0.2}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, and a CIE y chromaticity coordinate that was greater.

In the fourth populated row of Table 4, data is shown for the compound $(\text{Lu}_{0.77}\text{Gd}_{0.2}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, designated G1. This compound emits light with a peak wavelength at about 550 nm, the shortest wavelength of the group of compounds

listed in Table 4, excepting YAG1. It also displays a chromaticity coordinate, CIE x, that is the lowest of the group. The CIE y coordinate of this compound was the highest of the group. A similar compound containing Gd, with no Tb, but with higher levels of Gd, designated G3, emitted light at the highest peak wavelength of the group. This compound had the formula $(\text{Lu}_{0.47}\text{Gd}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. Comparing $(\text{Lu}_{0.47}\text{Gd}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ with the $(\text{Lu}_{0.47}\text{Tb}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ compound discussed earlier shows that the Gd-containing compound emits at a longer wavelength than does the Tb-containing compound, but the Tb-containing compound emits with a higher photoluminescent intensity.

The two compositions in Table 4 labeled “YAG1” and “YAG2” are based on yttrium (Y) rather than lutetium (Lu)—these Y-based compositions are included for comparison. They each have the approximate formula $(\text{Y}_{0.97}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. These compounds also emit within the range 550 nm to 560 nm.

The data from Table 4 may be shown graphically, as shown in FIGS. 18-20, which figures also show a blue light source (such as a GaN LED) used for exciting the phosphor compositions of the present invention—the blue light source and yellow phosphor providing a “white” light source. FIG. 18 is a plot of the photoluminescent intensity of two compounds labeled “G1” and “T1.” The former has a composition where the concentration of Gd is $x=0.2$, such that the formula is $(\text{Lu}_{0.77}\text{Gd}_{0.2}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. The peak emission wavelength is at about 550 nm. Here, the Gd containing compound ($x=0.2$, upper curve) has virtually identical photoluminescent intensity and peak emission wavelength as the sample labeled “T1” (lower curve).

The two compounds in FIG. 19 have about the same photoluminescent intensity as the compounds in FIG. 18, but the peak emission wavelengths in FIG. 19 are shifted slightly to longer wavelengths. The upper graph in FIG. 19 is “T2,” and it has a Tb concentration of $x=0.5$, such that its composition is $(\text{Lu}_{0.47}\text{Tb}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. The lower curve in FIG. 19 is the sample “G2,” and it has a Gd concentration of $x=0.3$, such that its composition is $(\text{Lu}_{0.67}\text{Gd}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. When these two compounds are compared, one sees that the Tb containing compound ($x=0.5$) has a slightly higher photoluminescent intensity than the “G2” compound, and a very slightly shorter peak emission wavelength.

Compounds with slightly longer wavelengths of emission, relative to FIGS. 19 and 18, are shown in FIG. 20. Referring to FIG. 20, the upper curve in the graph corresponds to the sample labeled “TG1,” where the Gd concentration is 0.2 and the Tb concentration is 0.3, such that the phosphor has the formula $(\text{Lu}_{0.47}\text{Gd}_{0.2}\text{Tb}_{0.3}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. The lower curve in the graph corresponds to the sample labeled “G3,” where the Gd concentration is 0.5. This compound has no Tb, so the formula is $(\text{Lu}_{0.47}\text{Gd}_{0.5}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. Here, the compound containing both Gd and Tb displays a higher

photoluminescent intensity than the compound containing the same amount of rare earth ($x=0.5$) but in the form of Gd-only; the Tb and Gd containing compound emits at a slight shorter wavelength than the Gd-only compound.

The effect of changing either the Gd concentration or the Tb concentration in a compound having the general formula $(\text{Lu}_{0.97-x}\text{A}_x\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$, is shown in FIG. 21. (In this experiment, A is either Gd or Tb, but it is emphasized that according to embodiments of the present invention, Gd and Tb may be present either individually or in combinations.) Referring to FIG. 21, one skilled in the art may observe that increasing the Gd concentration from $x=0$ to $x=0.5$ causes the peak emission wavelength to increase more rapidly than did the peak emission wavelength for compounds in a series where the Tb concentration was increased from about $x=0$ to about $x=1.0$. Stated another way, to render the emission wavelength to increase from about 542 nm (where the phosphor contains only Lu at $x=0$) to about 562 nm, it was necessary to completely replace all of the Lu with Tb ($x=1$ for Tb), whereas this wavelength increase was achieved at a concentration of Gd at half that value ($x=0.5$, so that only half of the Lu has been replaced in the Gd series).

The relationship between photoluminescent intensity and peak emission wavelength that the Gd-containing series of compounds have, versus the Tb-containing series of compounds, is shown in FIG. 22. In this graph, relative photoluminescent intensity on the ordinate (y-axis) is plotted against peak emission wavelength (in nm, on the x-axis). For both series of compounds, the relative photoluminescent intensity decreases as the Gd or Tb concentration increases (and, concomitantly, as the peak emission wavelength increases), with photoluminescent intensity decreasing faster in the Gd-containing series of samples than in the Tb-containing samples.

The specific data used to compose the plots in FIGS. 21 and 22 is provided in Tables 5 and 6 above.

The thermal stability of exemplary Tb-containing, and Tb and Gd-containing compounds is shown in FIG. 23. Also shown for comparison are Gd-containing phosphor compounds containing Gd but no Tb. Referring to FIG. 23, the CIE y chromaticity coordinate is plotted on the y-axis against the CIE x chromaticity coordinate on the x-axis. The data points are collected at 20 degree temperature intervals from 20° C. to 220° C.—a temperature range that includes the operating temperatures of the phosphor materials for most applications. The data is shown in Tables 7(i) & 7(ii). A shift in CIE coordinates of less than 0.005 is preferred over the temperature range tested—it is notable that only the Tb-containing materials show a shift of CIE coordinates within this range for both x and y coordinates. Specifically, only T1, T2 and TG1 exhibit the preferred temperature stability. The better temperature stability of the terbium-containing phosphor materials compared with the phosphor materials with gadolinium and no terbium is an unexpected result.

TABLE 7(i)

Temperature dependence of CIE for Tb and Gd containing compounds						
Temperature (° C.)	G1		G3		T1	
	CIE X	CIE Y	CIE x	CIE y	CIE x	CIE y
20	0.4156	0.5483	0.4441	0.5344	0.4215	0.5454
40	0.4163	0.5479	0.444	0.5342	0.4218	0.5447
60	0.4165	0.5477	0.4446	0.5347	0.4227	0.5449
80	0.4167	0.5474	0.4451	0.5352	0.4229	0.5447
100	0.4187	0.5492	0.4442	0.5353	0.4226	0.544

TABLE 7(i)-continued

Temperature dependence of CIE for Tb and Gd containing compounds						
Temperature (° C.)	G1		G3		T1	
	CIE X	CIE Y	CIE x	CIE y	CIE x	CIE y
120	0.4185	0.5492	0.4432	0.5354	0.4244	0.5456
140	0.4182	0.5493	0.4438	0.5359	0.4243	0.546
160	0.4175	0.5495	0.4429	0.5364	0.4241	0.546
180	0.4191	0.5515	0.442	0.5369	0.42365	0.5461
200	0.4182	0.5531	0.4399	0.5381	0.4232	0.5462
220	0.4174	0.5534	0.4408	0.5395	0.4226	0.5462
MAX Change	Δ CIE X =	Δ CIE Y =	Δ CIE X =	Δ CIE Y =	Δ CIE X =	Δ CIE Y =
	0.0035	0.0060	0.0043	0.0053	0.0021	0.0022

15

TABLE 7(ii)

Temperature dependence of CIE for Tb and Gd containing compounds				
Temperature (° C.)	T2		TG1	
	CIE x	CIE y	CIE x	CIE y
20	0.4357	0.5375	0.4444	0.5325
40	0.4379	0.5379	0.4451	0.5322
60	0.4385	0.5373	0.4454	0.5318
80	0.4384	0.5364	0.4458	0.5321
100	0.4395	0.537	0.4455	0.5319
120	0.4388	0.5364	0.4449	0.5322
140	0.4392	0.5366	0.4457	0.5333
160	0.4389	0.5366	0.4462	0.5335
180	0.4384	0.5365	0.4461	0.5342
200	0.4381	0.5366	0.4449	0.5344
220	0.4404	0.5385	0.4455	0.5351
MAX Change	Δ CIE X =	Δ CIE Y =	Δ CIE X =	Δ CIE Y =
	0.0047	0.0020	0.0018	0.0033

20

25

30

In another embodiment of the present invention, the phosphor comprises a cerium-activated, yellow-green to yellow-emitting aluminate-based phosphor represented by the formula $(\text{Lu}_{0.97-x}\text{A}_x\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$. Here, A is at least one rare earth selected from the group consisting of Gd and Tb; and x ranges from about 0.001 to about 1.0. As with the embodiment disclosed in the previous paragraph, this phosphor also contains at least some Tb.

Although the present invention has been particularly described with reference to yellow-green to yellow emitting aluminate-based phosphors, the teaching and principles of the present invention apply also to phosphors in which the Al has been replaced, in whole or in part, by Ga, Si or Ge—for example, silicate-, gallate- and germanate-based phosphors.

The embodiments of the phosphor materials containing halogens may have the halogen: (1) contained within the crystal substitutionally; (2) contained within the crystal interstitially; and/or (3) contained within grain boundaries that separate crystalline grains, regions and/or phases.

According to further embodiments of the present invention, the Lu aluminate materials in Table 8 have been made and tested, as described above. An example is provided of a representative procedure for making a compound with the formula $(\text{Lu}_{1-y}\text{Ce}_y)_3\text{Al}_5\text{O}_{12}$. Lu_2O_3 (272.664 g), CeO_2 (7.295 g), Al_2O_3 (120.041 g) and a flux (20.000 g) are mixed for between 4 and 20 hours with a mixer and then added to a crucible. The crucible is placed into a continuous furnace and sintered at between 1500° C. and 1700° C. for between 2 and 10 hours under reduced atmosphere. The sintered material is converted into a powder with a crushing machine. The powder is washed with acid and deionized water and then dried at between 120° C. and 180° C. for between 12 and 24 hours in an oven. Finally the powder is sieved through a 20 μm mesh to provide $\text{Lu}_{2.945}\text{Ce}_{0.055}\text{Al}_5\text{O}_{12}$ and characterized (i.e., emission wavelength, intensity, and CIE values, particle size distribution, etc.).

It is noted that the principles, embodiments, and concepts discussed in the present disclosure may be applied to this section that features terbium (Tb) and gadolinium (Gd). For example, in one embodiment of the present invention, the phosphor may comprise a cerium-activated, yellow-green to yellow-emitting aluminate-based phosphor having the formula $(\text{Lu}_{1-x-y}\text{A}_x\text{Ce}_y)_3\text{B}_z\text{Al}_5\text{O}_{12}\text{C}_{2z}$; where A is at least one of Sc, La, Gd, and Tb; B is at least one of Mg, Sr, Ca, and Ba; C is at least one of F, Cl, Br, and I; $0.001 \leq x \leq 1.0$; $0.001 \leq y \leq 0.2$; and $0 \leq z \leq 0.5$, and the phosphor in this embodiment contains at least some Tb.

In another embodiment of the present invention, the phosphor comprises a cerium-activated, yellow-green to yellow-emitting aluminate-based phosphor having the formula $(\text{Lu}_{1-x}\text{A}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$, where A is at least one rare earth selected from the group consisting of Gd and Tb, either individually or in combinations; x ranges from about 0.001 to about 1.0; and the phosphor contains at least some Tb.

TABLE 8

Further examples of green and yellow lutetium aluminate phosphors						
#	Composition	CIE _x	CIE _y	Emission Peak (nm)	Relative PL Intensity	D50 (μm)
1	$\text{Lu}_{2.70}\text{Gd}_{0.21}\text{Ce}_{0.09}\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.3}$	0.424	0.543	554	114	12
2	$\text{Lu}_{2.40}\text{Gd}_{0.51}\text{Ce}_{0.09}\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.3}$	0.453	0.525	565	111	11
3	$\text{Lu}_{1.92}\text{Gd}_{0.99}\text{Ce}_{0.09}\text{Ba}_{0.15}\text{Al}_5\text{O}_{12}\text{F}_{0.3}$	0.480	0.505	576	101	10
4	$\text{Lu}_{2.82}\text{Gd}_{0.09}\text{Ce}_{0.09}\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$	0.413	0.555	551	132	16
5	$\text{Lu}_{2.70}\text{Gd}_{0.21}\text{Ce}_{0.09}\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$	0.429	0.545	555	138	13
6	$\text{Lu}_{2.52}\text{Gd}_{0.39}\text{Ce}_{0.09}\text{Sr}_{0.34}\text{Al}_5\text{O}_{12}\text{F}_{0.68}$	0.436	0.537	558	122	14
7	$\text{Lu}_{2.975}\text{Ce}_{0.025}\text{Al}_5\text{O}_{12}$	0.327	0.578	515	135	13
8	$\text{Lu}_{2.97}\text{Ce}_{0.03}\text{Al}_5\text{O}_{12}$	0.334	0.577	520	135	13

TABLE 8-continued

Further examples of green and yellow lutetium aluminate phosphors					
#	Composition	CIE _x	CIE _y	Emission Peak (nm)	Relative PL Intensity D50 (μm)
9	Lu _{2.965} Ce _{0.035} Al ₅ O ₁₂	0.340	0.576	525	135 13
10	Lu _{2.96} Ce _{0.04} Al ₅ O ₁₂	0.347	0.573	530	135 13
11	Lu _{2.96} Ce _{0.04} Al ₅ O ₁₂	0.354	0.573	530	115 5.5
12	Lu _{2.945} Ce _{0.055} Al ₅ O ₁₂	0.354	0.569	534	137 13
13	Lu _{2.93} Ce _{0.07} Al ₅ O ₁₂	0.372	0.564	540	135 11
14	Lu _{2.84} Gd _{0.1} Ce _{0.06} Al ₅ O ₁₂	0.392	0.556	543	135 14
15	Lu _{2.84} Gd _{0.1} Ce _{0.06} Al ₅ O ₁₂	0.395	0.555	545	130 10
16	Lu _{2.84} Gd _{0.1} Ce _{0.06} Al ₅ O ₁₂	0.393	0.557	545	120 7
17	Lu _{2.64} Gd _{0.3} Ce _{0.06} Al ₅ O ₁₂	0.415	0.549	550	135 13
18	Equal proportions of: Lu _{2.64} Gd _{0.3} Ce _{0.06} Al ₅ O ₁₂ and Lu _{2.44} Gd _{0.5} Ce _{0.06} Al ₅ O ₁₂	0.431	0.540	555	125 13
19	Lu _{2.44} Gd _{0.5} Ce _{0.06} Al ₅ O ₁₂	0.447	0.532	560	120 13

According to further aspects of the invention, a white light illumination system may comprise: an excitation source with emission wavelength within a range of 200 nm to 480 nm; at least one of a red-emitting phosphor or a green-emitting phosphor; and a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor comprising terbium, wherein the phosphor is configured to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm. (See above for examples of the specific compounds that meet this requirement and also for examples that further meet the requirement that follows.) Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may be configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm. Yet furthermore, the red-emitting phosphor may have an emission wavelength within a range of 600 nm to 660 nm. Furthermore, the green-emitting phosphor may have an emission wavelength within a range of 500 nm to 545 nm. Yet furthermore, the red-emitting phosphor may be a nitride. Furthermore, the nitride may be at least one of (Ca,Sr)AlSiN₃:Eu²⁺, (Ca,Sr)₂N₅N₈:Eu²⁺, and (Ca,Sr)AlSi₄N₇:Eu²⁺. Yet furthermore, the green-emitting phosphor may be a silicate. Furthermore, the silicate may have the formula (Sr,Ba,Mg)₂SiO₄:Eu²⁺.

According to some embodiments, a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may have the formula (Lu_{1-x}Tb_x)₃Al₅O₁₂:Ce, wherein x ranges from about 0.1 to less than 1.0 and wherein the phosphor is configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm, and to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm. Furthermore, x may range from about 0.3 to less than 1.0. Furthermore, the excitation radiation may have a wavelength ranging from about 420 nm to about 480 nm. Furthermore, the formula may be (Lu_{0.97-x}Tb_xCe_{0.03})₃Al₅O₁₂:Ce. Furthermore, x may be in the range of 0.3 to 0.5, endpoints inclusive. Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may include the rare earth element gadolinium (Gd). Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may include the rare earth element gadolinium (Gd) and the formula may be (Lu_{1-x-y}Tb_xGd_y)₃Al₅O₁₂:Ce, wherein x ranges from about 0.1 to less than 1.0, y is greater than zero, and x+y<1. Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may include

the rare earth element gadolinium (Gd) and the formula may be (Lu_{0.97-x-y}Tb_xGd_yCe_{0.03})₃Al₅O₁₂, wherein y is greater than zero and x+y<1, and in some embodiments x=0.3 and y=0.2. Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may include a halogen. Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may include a halogen contained within the crystal substitutionally. Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may include a halogen contained within the crystal interstitially.

According to some embodiments, a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may have the formula (Lu_{1-x}Tb_x)₃A_zAl₅O₁₂C_{2z}:Ce, wherein: A is at least one of Mg, Sr, Ca, and Ba; B is at least one of F, Cl, Br, and I; 0.001≤x<1.0; and 0<z≤0.5. Furthermore, the yellow-green to yellow-emitting aluminate-based phosphor may further include the rare earth element gadolinium (Gd).

According to some embodiments, a white light illumination system may comprise: an excitation source with emission wavelength within a range of 200 nm to 480 nm; at least one of a red-emitting phosphor or a green-emitting phosphor; and a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor comprising terbium, wherein the phosphor is configured to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm. Furthermore, the cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor may be configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm. Furthermore, the red-emitting phosphor may have an emission wavelength within a range of 600 nm to 660 nm. Furthermore, the green-emitting phosphor may have an emission wavelength within a range of 500 nm to 545 nm. Furthermore, the red-emitting phosphor may be a nitride, and in some embodiments the nitride may be at least one of (Ca,Sr)AlSiN₃:Eu²⁺, (Ca,Sr)₂N₅N₈:Eu²⁺, and (Ca,Sr)AlSi₄N₇:Eu²⁺. Furthermore, the green-emitting phosphor may be a silicate, and in some embodiments the silicate has the formula (Sr,Ba,Mg)₂SiO₄:Eu²⁺.

Although the present invention has been particularly described with reference to certain embodiments thereof, it should be readily apparent to those of ordinary skill in the art that changes and modifications in the form and details may be made without departing from the spirit and scope of the invention.

23

What is claimed is:

1. A cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor having the formula $(\text{Lu}_{1-x}\text{A}_x)_3\text{B}_z\text{Al}_5\text{O}_{12}\text{C}_w:\text{Ce}$ and wherein:

A is at least one of Gd and Tb;

B is at least one of Mg, Sr, Ca, and Ba;

C is at least one of F, Cl, Br, and I;

$0.001 \leq x \leq 1.0$;

$0 < z \leq 0.5$; and

$2z > w \geq 2zp$, wherein p is chosen from the group consisting of 0.50, 0.75, 0.90 and 0.95.

2. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein $2z > w \geq z$.

3. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein $2z > w \geq 1.5z$.

4. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein $2z > w \geq 1.8z$.

5. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein $2z > w \geq 1.9z$.

6. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein C is contained within the crystal substitutionally.

7. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein C is contained within the crystal interstitially.

8. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein

A is Tb.

9. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein:

B is at least one of Sr and Ba; and

C is F.

10. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein the yellow-green to yellow-emitting lutetium aluminate-based phosphor is configured to absorb excitation radiation having a wavelength

24

ranging from about 380 nm to about 480 nm, and to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm.

11. A white light illumination system comprising:

an excitation source with emission wavelength within a range of 200 nm to 480 nm;

at least one of a red-emitting phosphor or a green-emitting phosphor; and

a cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor comprising terbium of claim 1, wherein the phosphor is configured to emit light having a peak emission wavelength ranging from about 550 nm to about 565 nm.

12. The white light illumination system of claim 11, wherein said cerium-activated, yellow-green to yellow-emitting lutetium aluminate-based phosphor is configured to absorb excitation radiation having a wavelength ranging from about 380 nm to about 480 nm.

13. The white light illumination system of claim 11, wherein the red-emitting phosphor has an emission wavelength within a range of 600 nm to 660 nm.

14. The white light illumination system of claim 11, wherein the green-emitting phosphor has an emission wavelength within a range of 500 nm to 545 nm.

15. The white light illumination system of claim 11, wherein the red-emitting phosphor is a nitride.

16. The white light illumination system of claim 15, wherein the nitride is at least one of $(\text{Ca}, \text{Sr})\text{AlSiN}_3:\text{Eu}^{2+}$, $(\text{Ca}, \text{Sr})_2\text{N}_5\text{N}_8:\text{Eu}^{2+}$, and $(\text{Ca}, \text{Sr})\text{AlSi}_4\text{N}_7:\text{Eu}^{2+}$.

17. The white light illumination system of claim 11, wherein the green-emitting phosphor is a silicate.

18. The white light illumination system of claim 17, wherein the silicate has the formula $(\text{Sr}, \text{Ba}, \text{Mg})_2\text{SiO}_4:\text{Eu}^{2+}$.

19. The yellow-green to yellow-emitting lutetium aluminate-based phosphor of claim 1, wherein C is contained within the crystal at grain boundaries.

* * * * *